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Removal of emerging trace organic contaminants by nanofiltration and reverse osmosis

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Removal of Emerging Trace Organic Contaminants by Nanofiltration and Reverse Osmosis

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By

Long Duc Nghiem

Faculty of Engineering
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Certificate of Originality

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma at UoW or any other educational institution, except where due acknowledgment has been made in the text.

I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.

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Abstract

This study investigates the retention mechanisms of three prominent classes of emerging trace organic contaminants — natural steroid hormones, hormone mimicking compounds, and pharmaceutically active compounds — by several nanofiltration (NF) and reverse osmosis membranes. Laboratory-scale experiments were carried out using both cross flow and dead end stirred cell filtration equipment with the goal of relating trace organic retention behaviour to membrane characteristics, physicochemical properties of the trace organic molecules, and solution chemistry.

The results reported here show that retention of neutral trace organics by a tight NF or RO membrane is dominated by steric (size) exclusion, whereas both electrostatic repulsion and steric exclusion govern the retention of negatively charged trace organics by a loose NF membrane. In the latter case, speciation of trace organics may lead to a dramatic change in retention as a function of pH, with much greater retention observed for ionized, negatively charged trace organics. Retention of the negatively charged trace organics decreases as the solution's ionic strength increases due to charge shielding and double layer compression. For uncharged trace organic species, intrinsic physicochemical properties of the trace organic molecules can substantially affect their retention. In their neutral form, natural steroid hormones, hormone mimicking compounds, and pharmaceuticals such as ibuprofen adsorb considerably to the membrane because of their relatively high hydrophobicity. Similarly, polarity (represented by the dipole moment) can influence the separation of molecules that are cylindrical in shape as they can be directed to approach the membrane pores head on due to attractive interaction between the molecule polar centers and fixed charged groups on the membrane surface. This phenomenon is probably inherent for high dipole moment organic compounds and the governing retention mechanism remains steric in nature.

The adsorption of trace organics to the membrane polymer has several important implications. Firstly, because the adsorptive capacity of the membrane is limited, the final retention stabilizes when the adsorption of trace organics into the membrane polymer has reached equilibrium. At this later filtration stage, the overall hormone retention is lower than what expected based on solely size

exclusion mechanism. This behaviour is attributed to partitioning and subsequent diffusion of hormone molecules in the membrane polymeric phase, which ultimately results in a lower retention. Trace organic diffusion in the membrane polymeric matrix most likely depends on the size of the molecule, hydrogen bonding of the compound to membrane functional groups, and hydrophobic interactions of the compound with the membrane polymeric matrix. Secondly, the membrane can serve as a large reservoir for trace organics and their release may be possible during membrane cleaning or erratic pH variation during operation. Treatment of membrane cleaning solution should be carefully considered when such trace organics are amongst the target contaminants in NF/RO membrane filtration.

The study also critically demonstrates the possible complexity of a real membrane filtration system where trace organic contaminants are of concern. Several factors including operating conditions, the solution chemistry, and other constituents such as organic and particulate matter that may be present in the feed solution can influence the filtration of trace organics. Findings in this study are crucial in understanding the removal mechanisms and filtration processes of trace organic contaminants. However, the application of such findings to a practical situation requires a careful consideration of these factors.

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Mum and Dad, thank you for having me.

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Chapter 1

Introduction

The development of membrane technology

Membrane filtration has emerged as a technology of choice in the water industry. It has numerous advantages over conventional treatment technology. These include small footprint, low or almost zero chemical consumption, capability to upscale and retrofit to existing facility with ease or to combine with other treatment processes to maximise treatment efficiency, and most of all, superior product water quality. Over time, problematic technical and economical drawbacks associated with membrane technology such as membrane fouling, energy consumption, and limited membrane lifetime have been progressively addressed. Consequently, the size and number of membrane filtration applications in the water industry have sky-rocketed over the last few years. Although the shear phenomenal development in such a short time makes it difficult to determine whether membrane filtration is truly a mature or still an emerging technology, it is certain that (at least at the time of this dissertation) membrane technology is facing a new challenge, which is the removal of emerging water and wastewater contaminants.

Emerging trace organic contaminants

Although the occurrence and fate of trace contaminants in the aquatic environment has long been recognised as an important issue of public health and environmental concern, only recently this issue has truly captured the scientific spot light. This is attributed to the increasingly stringent water quality regulation, significant advance in analytical techniques, and above all a paradigm shift towards water reclamation (or water recycling as it is called in Australia). Indeed, most emerging water and wastewater contaminants are of anthropogenic origin and can enter the environment either directly or indirectly via the sewer. However, conventional wastewater treatment plants (WWTPs) are not designed to eliminate them.

The capacity of conventional WWTPs to remove trace organic contaminants depends essentially on the biological treatment stage, where trace organic contaminants are removed by sorption to

suspended solids and by biological degradation. Removal of several hydrophobic compounds has been reported to be positively correlated to the sludge retention time (SRT), with an SRT of at least 10 days being needed to achieve effective removal [1, 2]. However, many WWTPs in the United States and Europe are not designed with a long enough SRT to satisfy this requirement [2]. The low influent concentration of trace organic contaminants and seasonal temperature changes can further complicate the problem [1]. Some trace organics such as carbamazepine are highly persistent and have been proven to be inert to the biological treatment process [1, 3]. Consequently, removal efficiency of trace organic contaminants by conventional WWTPs varies greatly, but the overall removal can be quite low. Trace organic contaminants are ubiquitous in most secondary treated effluents and receiving freshwater bodies.

Trace contaminants can significantly undermine water quality from both a toxicological and a psychological point of view [2]. Several adverse health effects as a direct or indirect result of trace contaminant exposure have begun to emerge [4-7]. Although the full impact of these emerging trace contaminants on environmental health is still being intensely debated amongst the scientific world, removal of such contaminants has become a critical issue. Given the apparent difficulty in effectively removing certain trace contaminants from wastewaters by conventional means, scope exists for the use of membranes - particularly nanofiltration (NF) and low pressure reverse osmosis (RO) membranes - in improving their removal.

Recent progress

Both NF and RO are pressurised driven membranes, where an applied transmembrane pressure forces water through a semipermeable barrier with selective transport capacity to retain contaminants. The potential of these membrane filtration processes to remove trace organic contaminants was first demonstrated in 1975 [8]. To date, various studies have also reported a complete or near complete retention of organics with relatively small molecular weight [9-13]. However, most (if not all) of these studies are heavily focussed on the more traditional contaminants such as pesticides or other industrial synthetic organic compounds. Furthermore, the membrane was often treated as a black box and little attention was given to elucidate the actual transport processes within the membranes. Data obtained from these studies remained limited, clearly indicating that the transport theories in their general forms are unable to satisfactorily describe the separation of trace contaminants in NF/RO filtration processes. To date, the retention mechanisms of trace contaminants are still poorly understood.

Research objectives

A fundamental understanding of trace organic contaminant removal mechanisms by NF/RO membranes will markedly leverage the significance of these filtration processes in the water industry. The objectives of this study are to examine and delineate the removal mechanisms of emerging trace contaminants by NF/RO membranes. Three distinctive groups of emerging trace organic contaminants, namely natural steroid hormones, hormone mimicking compounds, and pharmaceutically active compounds were selected for investigation. These contaminants are ubiquitous in secondary treated effluent and most fresh water bodies and present a heightened concern over their adverse environmental health impact on both humans and wildlife. Experiments were carried out with ten commercially available NF/RO membranes. Their properties as well as the physicochemical properties of the trace contaminants were both carefully examined. This dissertation focused on the critical relationships between the physicochemical properties of the trace contaminants, membrane characteristics, and solution chemistry. Such relationships were investigated and delineated in detail. On the basis of these results, mechanisms of trace organic contaminant removal by NF/RO membranes were elucidated and discussed.

Dissertation structure

The structure of this dissertation is schematically described in Figure 1.1. The body of the dissertation consists of 7 chapters. Chapter 2 provides a comprehensive literature review on the current state of knowledge on trace contaminants removal using NF/RO membranes. The chapter includes up to date findings resulting from other studies, which were undertaken concurrently to this dissertation. Findings that have already been published as a result of this study were also selectively included to provide an up to date and comprehensive panorama of the topic. Detailed descriptions of the selected membranes, trace organics, as well as the filtration system and protocol used in this study are presented in Chapter 3. This is followed by a critical evaluation of four distinctive but interlocking filtration phenomena: steric interaction (Chapter 4), electrostatic interaction (Chapter 5), adsorption (Chapter 6), and sorption-diffusion (Chapter 7). The results were delineated to elucidate the removal mechanisms of trace contaminants by NF/RO membranes. In Chapter 8 an attempt is made to relate fundamental findings of this study to practical applications by investigating the solution matrix effects on the separation process of trace organic contaminants. The conclusion (Chapter 9) summarises critical and fundamental findings of this study. This dissertation ends with several concluding remarks (Chapter 10) on research outlook with regard to

this topic and suggestions for future research to further enhance the potential of membrane technology in dealing with trace organic contaminants.

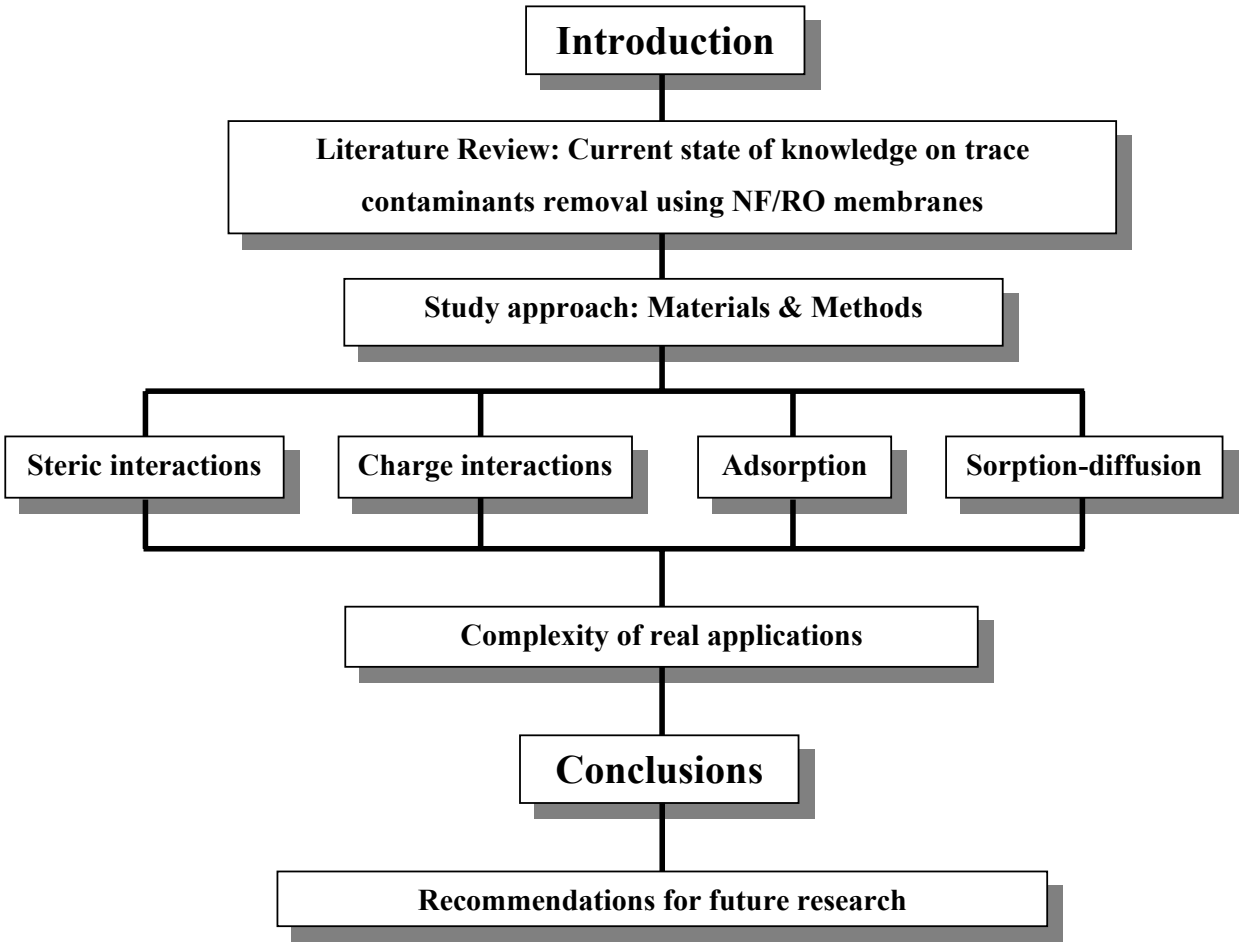


Figure 1.1: Schematic description of the "Removal of trace contaminants using membrane technology" dissertation structure.

Chapter 2

Literature Review: Current state of knowledge

1. Introduction

The occurrence and fate of both organic and inorganic trace contaminants in the aquatic environment has long been recognized as an important issue of public health and environmental concern. A wide range of trace organics, both synthetic and natural, have been detected and identified as important contaminants in sewage and effluent impacting on water bodies including surface and groundwater. Trace inorganic contaminants can also occur naturally in groundwater under certain geochemical conditions.

Trace contaminants are defined as chemicals of concern to human health and the biotic environment due to a combination of their physicochemical toxicological properties. In the aquatic environment, they are present at trace levels, usually in the μg/L range or less. From a toxicological point of view, low concentrations of trace contaminants in ground and drinking water may not always be harmful to humans (in fact the majority of health effects are unknown at this stage), but they are undesirable with regards to the "precautionary principle" [14]. Although trace contaminant removal is an issue facing various industries, this chapter focuses mostly on the water purification process. The role of nanofiltration (NF) and reveres osmosis (RO) membrane filtration processes in water and wastewater treatment, occurrence of trace contaminants and their environmental implications, separation processes and a review of current studies are presented in this chapter.

2. Nanofiltration in water and wastewater treatment

Historically, nanofiltration (NF) and reverse osmosis (RO) were primarily applied in water softening and desalination. However, NF has recently found its niche in both water and wastewater industries. This can be attributed to at least three factors [15]:

- More stringent regulation for both potable and waste waters;
- Increasing demand for water; and
- Market self-regulation.

Given the increasing difficulty in remaining under the maximum contaminant levels (MCLs), there has been a shift from enhanced coagulation to membrane filtration in both water and wastewater treatment [16]. While coagulants preferentially remove larger molecular weight (MW) compounds, which tend to be more hydrophobic, it is more difficult to remove the smaller and more hydrophilic compounds by chemical means. NF membranes have a significant potential in retaining organics and hence are used increasingly for treatment of "coloured" waters. Increasing demand for water has led to the exploitation of resources of lower water quality that are not suitable for conventional treatment. Indeed, water recycling has now become a major approach to replenishing diminishing water resources [17, 18].

Table 2.1: Examples of wastewater and water treatment plants using NF/RO membranes.

	Location	Capacity (m^3/d)	Application
Water reuse	Water Factory 21 (Orange County California) [19]	330 000	Indirect potable reuse via groundwater recharge
	Mexico City [20]	500	Irrigation
	City of Livermore (California) [20]	2 800	Irrigation; fire fighting water
	Chandler (Arizona) [20]	4 160	Indirect potable
	Artis Zoo (Amsterdam) [21]	430-1 200	Cleaning animals cages; Ecoflow for the zoo environment
	Sydney Olympic Park (Homebush Bay-Sydney) [22]	2200	Non-potable reuse
	Kranji NEWater plant (Singapore) [23]	40 000	Indirect potable reuse
Water supply	Mery-Sur-Oise (Paris, World's largest water supply plant using NF process) [24]	140 000	Pesticide removal for drinking water supply

The majority of wastewater organics are the remnants of biological treatment and tend to be lower in molecular weight and aromaticity than organics found in natural waters [25]. These compounds are also referred to as effluent organic matter (EfOM) [25]. Further, such compounds may be less biologically degradable due partly to their binding capacity to bulk organic matter [26, 27] and contain a large number of trace organics. Finally, market self-regulation has assisted the membrane process becoming an economically viable option due to the development and commercialisation of

membrane technologies and the water industries themselves. Examples of wastewater and water treatment plants using NF/RO membranes are shown in Table 2.1.

NF is also an effective method to treat landfill leachate which may contain a wealth of trace contaminants that are not biodegradable and will thus remain in the water discharged after undergoing biological treatment [28]. In addition, NF plays an important role in some small-scale operations including mobile water treatment units for military activities in remote regions from the worst sources such as raw sewage [14] and space travel [29]. In the course of military action, a reliable and safe drinking water supply is an important logistical concern and it may be necessary to produce water from highly contaminated sources that may contain many trace contaminants. Safe and reliable direct water reuse is also a priority for long missions in space. Last but not least, NF presents a valuable tool for researchers to concentrate and characterize a variety of organics from aquatic environments [30, 31].

The removal processes of trace contaminants using NF are complex and to date are poorly understood. Hence the mechanisms in this chapter are preliminary and much work still needs to be done to fill in the knowledge gap. This chapter will document and discuss the significance of trace contaminants in water and wastewater applications where NF can be applied as a treatment process. Removal mechanisms and membrane-contaminant interactions are discussed.

3. *Occurrence of trace organics and their effects on health & environment*

Organic compounds are ubiquitous in any aquatic environment. Organic matter found in water spans a wide spectrum, with molecular weights ranging from several thousand to less than a hundred Daltons. Most compounds on the upper end of this spectrum are of natural origin, and they are commonly known as natural organic matter (NOM). Although they are not considered harmful to human health, the formation of carcinogenic trihalomethanes (THMs) and other disinfection by-products after disinfection is directly related to the amount of these precursor compounds present.
Trace organics are generally located at the lower end of this spectrum. It is the lower molecular weight compounds that are of significant concern. Some trace organics such as pesticides, trihalomethanes (THMs), polychlorinated biphenols (PCBs) and polyaromatic hydrocarbons (PAHs) are regulated. That is, maximum contamination levels (MCLs) are established as enforceable standards by a regulatory authority. However, the list of regulated compounds is not exhaustive. Many compounds have not yet been regulated due to difficulties associated with

analysis of such compounds at trace levels, categorization or identification and proof of health effects or dose response relationships.

Table 2.2: Groups of trace contaminants, definitions and examples

Group	Definition	Examples	US-EPA MCL in drinking water (μg/L)[32]
DBPs	By-products resulting from interaction of disinfectants (chlorine, chloramines, ozone, etc) with naturally occurring organic material such as humic and fulvic acids during disinfection	Bromate	10
		Chlorite	1000
		Haloacetic acid (HAA5)	60
		Total trihalomethanes (THMs)	80
POPs	Synthetic organic compounds that are persistent, bioaccumulating and toxic organic compounds prone to long-range atmospheric transport	PCBs	0.5
		HCH (include Lindane)	0.2
		Dioxin (2,3,7,8-TCDD)	0.00003
Pesticides	Chemicals used as pesticides, insecticides, fungicides or herbicides	Heptachlor	0.4
		Lindane	0.2
		Endrin	2
		Atrazine	3
EDCs	Exogenous substances that cause adverse health effects in an intact organism, or its progeny, consequent to endocrine function [33]	Estrodiol	not regulated
		Estrone	not regulated
		PCBs	0.5
		Nonylphenol	not regulated
PhACs	Unused, residue or metabolites of pharmaceuticals that are administered to humans or animals for various benefit including treatment and prevention of diseases [34]	Ciprofloxacin	not regulated
		Iopamidol	not regulated
		Ioxithalamic acid	not regulated
		Carbamazepine	not regulated

Most trace contaminants are of anthropogenic origin. A variety of synthetic organics are produced in a substantial quantity each day for numerous beneficial uses such as pesticides, pigments, dye

carriers, preservatives, pharmaceuticals, refrigerants, propellants, heat transfer medium, dielectric fluid, degreasers, lubricants, etc. [35]. These compounds are collectively known as synthetic organic compounds (SOCs). Although, there is no doubt that SOCs have contributed to the prosperity of the world by increasing productivity in both industrial and agriculture activities, treating and preventing many diseases, they also present a significant environmental threat to mankind and biodiversity. The production of such chemicals may also entail the introduction of by-products and their metabolites, some of which are far more detrimental to human health and the environment than the parent compounds.

Depending on their characteristics, SOCs can be further divided into different groups including persistent organic compounds (POPs), pesticides, pharmaceutically active compounds (PhACs), and endocrine disrupting chemicals (EDCs). It is noteworthy that a contaminant can belong to more than one group. In fact, the last group includes several pesticides and PhACs. It also includes a number of naturally occurring compounds, which are excreted into the environment by humans, animals and plants. Definitions and example compounds in these groups are presented in Table 2.2.

Guidelines and regulations with regard to trace contaminants in drinking and surface water are not uniform among authorities around the world. A framework for the regulation of EDCs and PhACs in the aquatic environment is currently being developed by the European Union and their counterparts (Australia and Israel). The US Geological Survey has published a list of emerging pollutants in natural waters [36].

Although the toxicology of several SOCs is well known, monitoring and especially treatment of such compounds have not been a focus in the water industry until late in the 90s. This stems from the fact that when drinking water standards were developed, water resources were assumed to be "pollution free" [37]. This assumption is becoming more and more questionable as indeed there are many pathways in which trace organics can reach water bodies. For example, contaminants may be directly applied to control waterborne diseases, derived from leaching contaminants off agriculture land, spray drift from agricultural operations (i.e. pesticides) and atmospheric fall out (i.e. DDT, PCBs), accidentally released into water bodies, discharged from chemical factories or contamination of water sources from sewer discharge-as is the case in many European rivers, for example, which receive effluent but also serve as a water supply.

On the other hand, studies on the removal of PhACs and EDCs are still very limited due to the absence of regulations as discussed above, but are experiencing a strong interest at present in part because of the increased need for water recycling and the uncertainties evolving around trace contaminants.

3.1 Disinfection by products

It is of paramount importance to ensure that drinking water is free of pathogenic microorganisms, which can cause disease and death. It is also desirable to eliminate or inactivate such microorganisms from sewage effluent prior to discharge into receiving water. Consequently, disinfection is one of the most important tools to achieve this goal. Disinfection can be accomplished via a variety of disinfectants or physical methods. Chlorine and hypochlorite are the most commonly used chemical disinfectants, however water may also be disinfected with chloramine, chlorine dioxide, ozone, ultraviolet radiation (UV) and physical processes such as ultrafiltration (UF) or NF. Unfortunately, disinfection processes (except membrane filtration) can produce a number of disinfection by products (DBPs), which may induce various forms of cancer and other health consequences [38-40].

Chlorine is the most common disinfectant, and in the chlorination process it reacts with NOM to produce a complex mixture of by-products, including a wide variety of halogenated compounds, with the main by-products being trihalomethanes (THMs) and halogenated acetic acids (HAAs). Other disinfectants can produce different types of by-products. For example, ozone is known to produce a variety of aldehydes [41]. It is possible, however, that other disinfection by-products, for which no health data are available, are present at extremely low concentrations. It is also possible that the combined effects of these compounds (both known and unknown) on health may be different to the individual effects. Nonetheless, the immediate health risks posed by disinfection by-products are considerably less than the long term exposure (or chronic) risks due to the presence of pathogenic microorganisms in water, which has not been disinfected. Hence, efforts to reduce the DBP concentration must not compromise disinfection itself but DBP formation and removal needs to be considered as part of disinfection.

While there are several methods to reduce the concentration of disinfection by-products such as disinfectant dosage optimization, NF is presented as a powerful tool to minimize DBP concentrations in finished water. Natural organic matter comprises a large fraction of macro-organics with high molecular weight. Therefore, NF can effectively eliminate DBPs by removing

natural occurring organic matter prior to disinfection. In such circumstances, reduction of DBP formation potential is commonly reported to indicate the effectiveness of DBPs removal. NF can also directly remove DBPs following disinfection. However, it is less effective as DBPs are organic compounds that are small in molecular weight. Indeed, in some cases, low-pressure RO membranes can be employed to ensure high removal rate of DBPs following disinfection. Table 2.3 summarises DBPs and DBP formation potentials reductions by NF from several studies.

Table 2.3: Reduction of DBPs and DBP formation potentials by various NF membranes (*THMFP: Trihalomethanes formation potential; TOXFP: Total organic halides formation potential; TOX: Total organic halides)

Membrane	Compound*	Formula	Retention (%)	Reference	Remark
NF70	THMFP	-	90-95	[42]	
	TOXFP	-	87		
Unknown	THMFP	-	95	[43]	Pilot scale
	TOXFP		93		
Unknown	Dibromochloropropane	$C_3H_5Br_2Cl$	35	[43]	Full scale
Unknown	Trichloromethane	$CHCl_3$	87	[44]	Full scale
	Bromodichloromethane	$CHBrCl_2$	87		
	Dibromochloromethane	$CHBr_2Cl$	70		
NF70	Tetrachloromethane	CCl_4	76-96	[45]	Lab scale
Polyamide	Dichloroacetic acid	$CHCl_2COOH$	68-71	[46]	Pilot scale
	Trichloroacetic acid	CCl_3COOH	82-84		
CDNF50	TOX	-	89-93	[47]	Bleaching paper mill effluent

While removal is generally high (mostly >80%), it depends on the contaminant type, the membrane used, operating conditions and especially the solution chemistry of the treated waters. Hence to date it is impossible to draw generic conclusions that are valid for all NF membranes and DBPs.

3.2 Persistent organic pollutants

In recent years persistent organic pollutants (POPs) have attracted significant attention from the scientific community as well as environmental policy makers and non-governmental organizations

such as Greenpeace [48-51]. Concern over recalcitrant and extreme toxic properties of these compounds has led to international efforts to control their use and disposal and to understand their global distribution and behaviour [52]. These efforts have resulted in the UN-ECE POP protocol signed by 36 countries including European countries, Canada and the United States of America [51]. UNEP has identified a list of 16 POPs, 11 of which are active ingredients of pesticides [53]. There are many more substances that may meet the POPs' criteria, which have yet to be declared due to difficulties associated with assessment of their toxicology and physicochemical properties [48].

3.3 Pesticides

As described above, pesticides are a dominant group in the list of POPs as defined by UNEP. The listed pesticides are DDT, aldrin, chlordane, dieldrin, endrin, heptachlor, mirex, toxaphene, and hexachlorobene [48].

Given their extreme environmental hazard, the use and production of persistent pesticides has ceased for at least two decades. However, traces of these substances are still detectable and applied in many regions throughout the world. Degradation of such compounds is slow [48], in the order of ten years or more for many substances, thus ambient levels of persistent pesticides in contaminated areas will decline only very slowly [52]. Consequently, the occurrence of persistent pesticides and their metabolites in surface water, groundwater and particularly reclaimed water are of concern to the water industry.

Although current registered pesticides are less persistent and harmful than their predecessors, the abundance of pesticides in both surface and ground water is common due to the widespread and long-term applications. Severe water quality changes caused by excessive application of pesticides have occurred, for example, in Europe and North America [54-58]. An intensive monitoring program conducted for three main rivers in the Paris area from 1991 to 1994 has revealed high levels of atrazine [56]. Results of this study are represented in Figure 2.1 and more detail on the removal of atrazine using NF is described elsewhere.

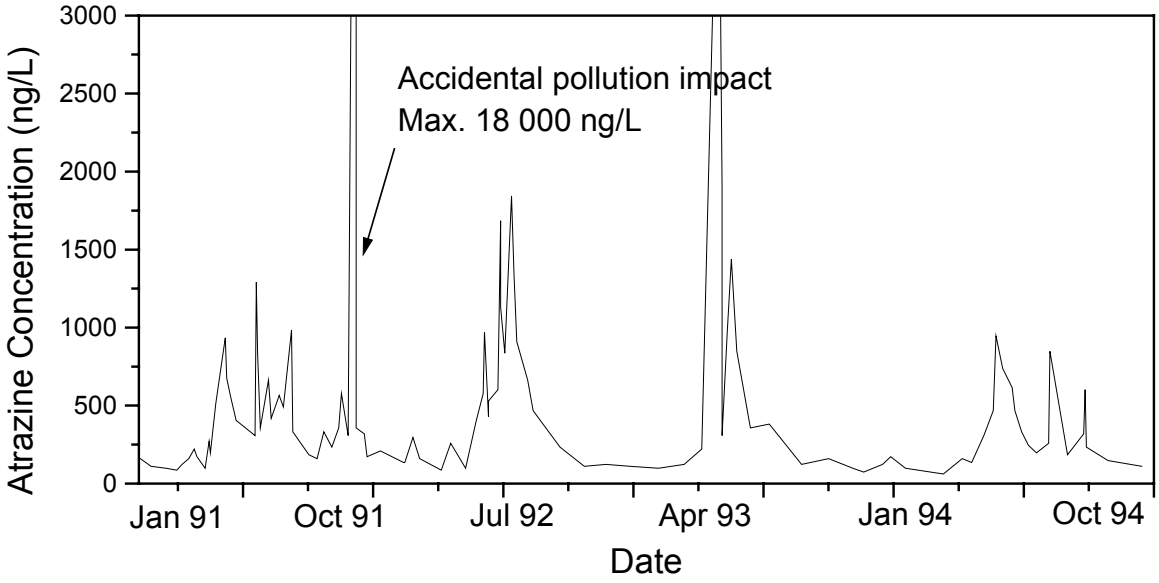
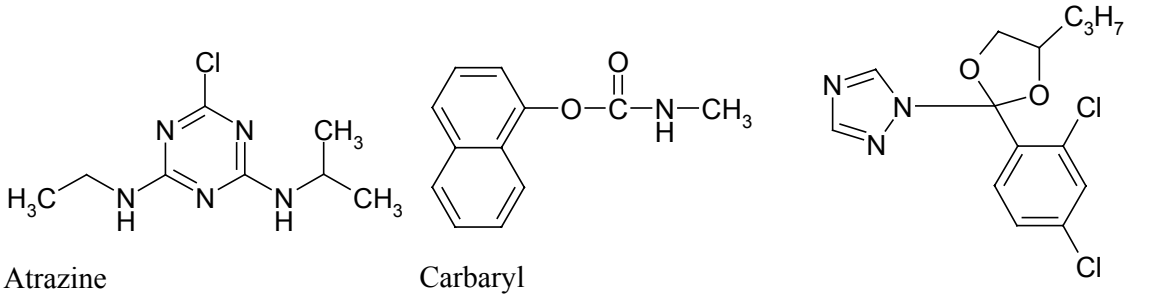


Figure 2.1: Atrazine concentration in the rivers of the Paris region from 1991 to 1994 [56].



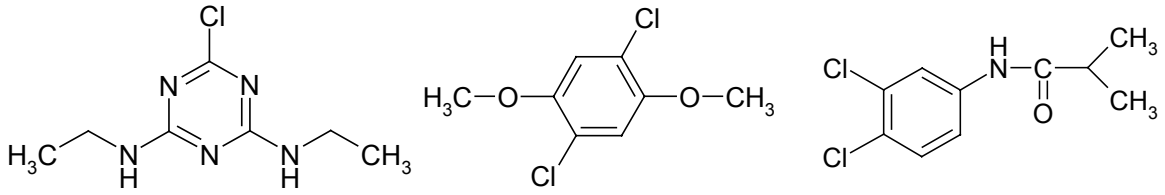


Figure 2.2: *Molecular structures of several pesticides.*

The problem is worse for developing countries due to intensive and widespread application of agriculture chemicals, weak and unenforceable regulations, and most of all low environmental awareness over the issue. Between 68 and 100% of tested drinking water sources were polluted with pesticides in 10 regions in Videira and Brazil when a study was carried out between June 1988 and December 1990 [59]. Organophosphorus pesticides were found at levels of 3 to 19 μg/L in groundwater and surface water in Egypt [59]. Water samples taken from the Bhopal area of India in 1990 showed DDT level in the range of 3 to 22 mg/L [60]. In some developing countries, there

exists evidence that DDT is still illegally used to combat mosquitoes despite a ban imposed by the government [61-63].

Table 2.4: Rejection of several pesticides by NF/RO membranes (*DCB: Dichlorobenzne, TCB: Trichlorobenzene).

Membrane	Compound*	Feed Conc. (µg/L)	Retention (%)	Reference	Remark
Unknown	1,4-DCB	0.16	56	[44]	Full scale
	1,2-DCB	0.20	50		
HNF-1	Simazine	20-170	42	[64]	Pilot scale
	Atrazine		61		
	Alachlor		89		
	Methoxychlor		99.2		
PVD 1	Diuron	1	82	[65]	Lab scale
	Simazine		92		
	Atrazine		92		
Desal 5 DK	Diuron	1	10		
	Simazine		38		
	Atrazine		47		
NF 200	Diuron	1	45	[66]	Lab scale, in distilled water
	Simazine		80		
	Atrazine		80		
NF 70	Simazine	0.1-0.4	50-100	[67]	Pilot scale, retention increases as NOM content varies from 0.4 to 3.6 mg/L DOC
	Atrazine	0.5-1	50-100		
NF 70	Simazine	300	96	[68]	Lab scale
	Atrazine	300	97		
NTR 7250	Carbaryl	500-1500	40	[69]	Lab scale
	Chloroneb		53		
	Propiconazole		98		
NTR 7410	Carbaryl		25		
	Chloroneb		99		

Given the resistance of these compounds to conventional water treatment, pesticide removal using NF and low-pressure RO membranes has been subject to intensive research. The results of several studies are shown in Table 2.4, illustrating the effectiveness of NF/RO membranes in removing such compounds using different membranes. Figure 2.2 shows molecular structures of several pesticides of particular environmental concern. Although molecular structures of most pesticides are branched (indicating a high retention by NF or low-pressure RO membranes), there is a great variation in both molecular structure and functional group amongst pesticides. In addition, the retention also strongly depends on the membrane used. For example, for atrazine retention values between 47 and 100% have been reported. From those results it is clear that one cannot generalise on the performance of NF to retain such contaminants.

3.4 Endocrine Disrupting Chemicals (EDCs)

The effects of endocrine-disrupting chemicals (EDCs) on both humans and the biota are of increasing concern. Over the last few years, intensive attempts have been made to study a wide variety of effects that have been attributed to EDCs. A multitude of environmental effects already observed include an increase in vittellogenin levels (a bio-indicator of feminity in fish) in male and juvenile female fish in and immediately downstream of sewage effluent discharge points [70-74]. More recent studies by many researchers have confirmed the impacts of EDCs on trout at typical concentrations encountered in sewage effluent [75-77].

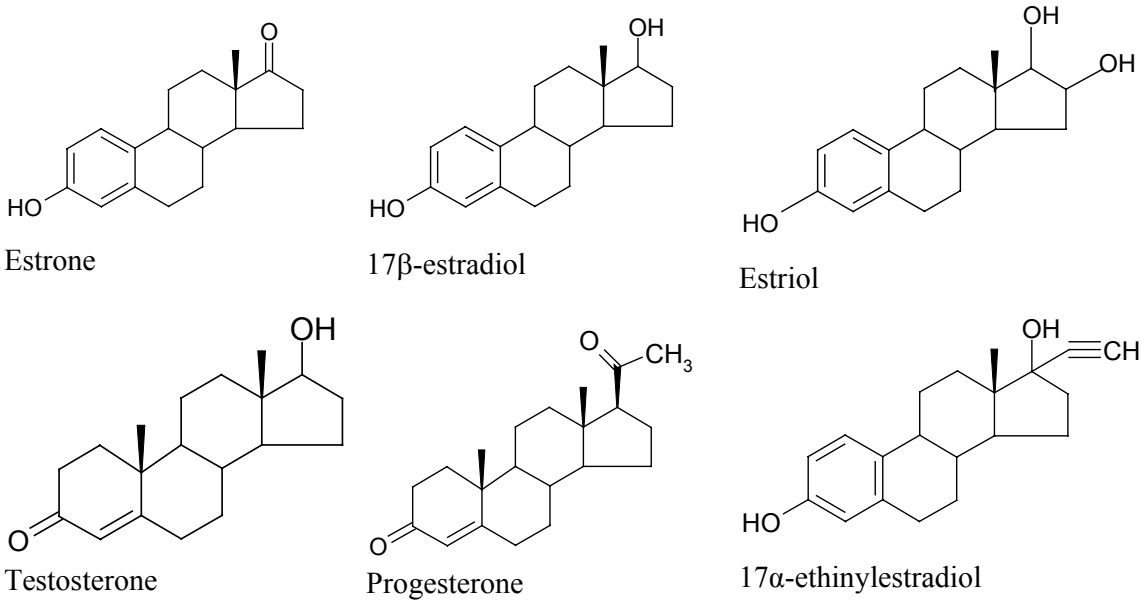


Figure 2.3: *Structures of several steroid hormones.*

EDCs consist of a vast number of both synthetic and natural organic as well as inorganic chemicals [7, 78, 79]. Amongst them, the impacts of steroid hormones such as estrone and 17β-estradiol (natural hormones) and 17α-ethinylestradiol (a synthetic hormone, the main component of the contraceptive pill) are prominent as they have far higher endocrine-disrupting potency than other EDCs (see Table 2.5) and are very commonly found in municipal wastewaters. 17β-estradiol has the most endocrine-disrupting potency. At a concentration as low as 1 ng/L, 17β-estradiol may cause distinctive effects on fish [71] and this compound is used as a reference for the determination of endocrine-disrupting potency. The steroid hormones all share a distinctive, characteristic five-ring structure (see Figure 2.3). Estrone and estriol are intermediate metabolite products of 17β-estradiol, which is mainly produced in the ovaries of the placenta. 17β-estradiol controls the development of the secondary female sex characteristics in women and together with the gestagens, control the reproductive process [80]. Progesterone is a major gestagen, and testosterone is an important male hormone.

Table 2.5: Examples of endocrine disrupting potency in relation to 17β-estradiol

Substance	Relative potency	Reference
17β-Estradiol	1	[81]
Estrone	3×10^{-1}	
17α-Ethinylestradiol	1-10	[81, 82]
17β-Estradiolglucuronide	2.5×10^{-2}	[82]
Diethylstilbestrol	7×10^{-2}	
Progesterone	2×10^{-2}	
Testosterone	1×10^{-2}	
Phytoestrogenes	$< 1 \times 10^{-3}$	
4-Butyl phenol	1.6×10^{-4}	[83]
4-Nonyl phenol	0.9×10^{-5}	
Kepone	1×10^{-6}	[84]
DDT	1×10^{-6}	

Being excreted by humans, such steroid hormones are ubiquitous in aquatic environments receiving sewage effluent. They are frequently detected in wastewater treatment plants (STP) discharge effluent or fresh water bodies receiving sewage effluent around the world within the lower ngL^{-1} range [36, 85-90]. Estradiol concentrations of up to 200 ngL^{-1} in STP effluent have been also

reported [78]. The performance of conventional wastewater treatment plants with regards to removal of steroid estrogens varies greatly and, as a consequence, concentrations of some steroid estrogens in secondary effluent often remain sufficiently high to harm wildlife such as fish [91]. In spite of the magnitude of this problem, research on the removal of EDCs (particularly steroid hormones) in water and wastewater has been limited to date due to their relatively low concentration and associated analytical difficulties, but has attracted significant interest in recent years, particularly in Europe where large projects such as POSEIDON and PTHREE are addressing these issues in great detail [85].

Table 2.6: Retention of estrone and 17β-estradiol using various NF/RO membranes.

Membrane	Compound	Feed Conc.	Retention (%)	Reference
UTC-20	17β-Estradiol	2 mg/L	75	[92]
	Estrone	2 mg/L	83	
ESNA	17β-Estradiol	27.1 μg/L	<10	[93]
XLE	17β-Estradiol	100 μg/L	83	[10]
SC-3100	17β-Estradiol	100 μg/L	29	
TFC-SR2	Estrone	100 ng/L	13	[94]
	17β-Estradiol	100 ng/L	21	
TFC-S	Estrone	100 ng/L	76	
	17β-Estradiol	100 ng/L	82	
X-20	Estrone	100 ng/L	87	
UTC60	Estrone	50 μg/L	80	[95]
	17β-Estradiol	50 μg/L	72	
NTR7250	Estrone	50 μg/L	57	
	17β-estradiol	50 μg/L	58	
PES10	Estrone	100 μg/L	40	[96]
	17β-estradiol	100 μg/L	50	

Given the potential impacts of EDCs such as estrone and 17β-estradiol, and inadequate and inconsistent performance of conventional wastewater treatment with regard to such compounds, NF and low-pressure RO membranes are likely to play an important role in removal of these compounds. Retention of estrone and 17β-estradiol using several NF/RO membranes reported by several recent studies are summarised in Table 2.6.

The results in Table 2.6 indicate that retention of the natural hormones estrone and 17β-estradiol also varies over a large range depending on the membrane type. However, the highest retention reported is 89% and hence a complete retention of those compounds cannot be achieved. This phenomenon will be explained in more detail in the later mechanisms section.

3.5 Pharmaceutically active compounds (PhACs)

Pharmaceuticals are administered to humans and animals for a variety of benefits including prevention and treatment of various types of disease. Given the variety of compounds in use and their widespread distribution and persistence in the environment, there are potential unanticipated consequences of pharmaceutical residues and their metabolites [97-99]. Most (if not all) pharmaceuticals administered to humans and animals are excreted to various degrees and discharged directly to the sewage system, depending upon the physiochemical properties of the compounds.

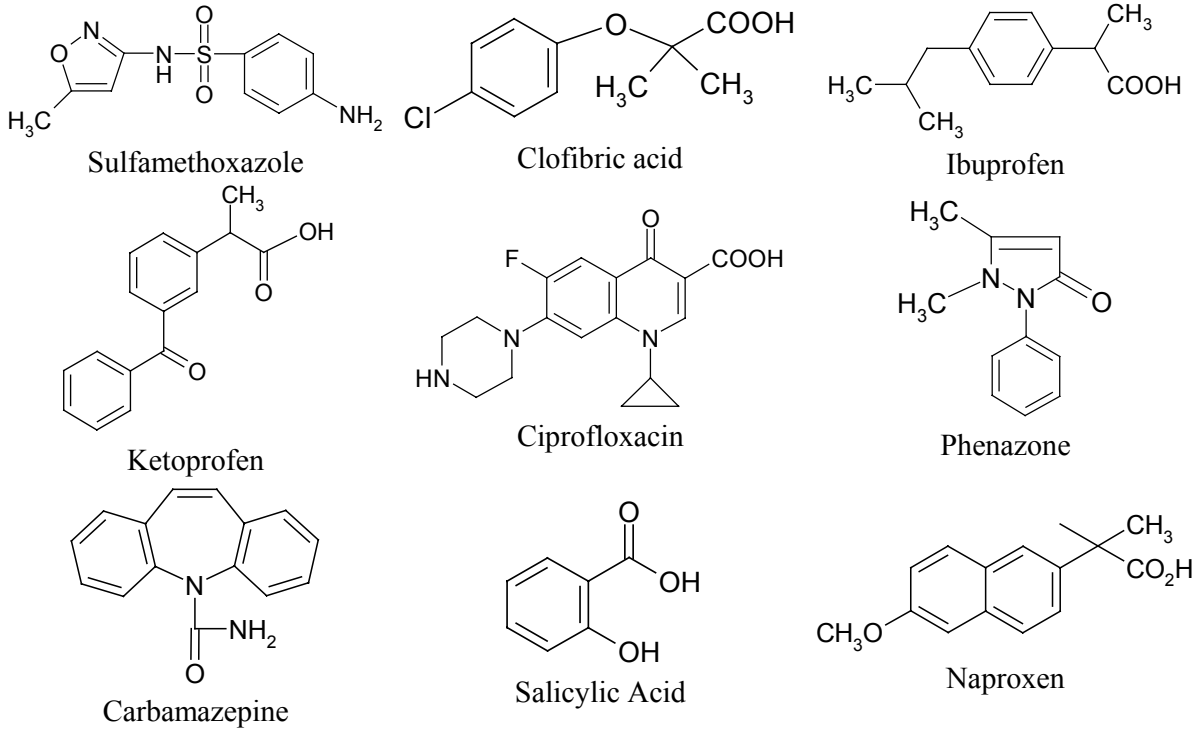


Figure 2.4: *Structures of several PhACs most frequently detected in aquatic environment.*

Although some of the compounds are biodegradable, most xenobiotics are persistent to the conventional biological sewage treatment process. Consequently, in investigations carried out in many countries including Austria, Australia, Brazil, Canada, Croatia, England, Germany, Greece, Italy, Spain, Switzerland, The Netherlands, and the U.S., more than 80 pharmaceuticals and their

metabolites, have been detected in aquatic environments at concentrations in the μg/L range or lower [34, 100-106]. Reported compounds include pharmaceuticals with a wide range of applications: analgesics, anti-inflammatory compounds, beta-blockers, lipid-regulators, antiepileptics, β_2-sympathomimetics, antineoplastics, antibiotics, X-ray media contrast agents and contraceptive drugs. Molecular structures of several PhACs frequently detected in the aquatic environment are shown in Figure 2.4.

As pharmaceuticals are designed to be biologically active, their potential to affect a large variety of non-target organisms for a wide range of physiological consequences is inherent. The potential for induction [107] or proliferation of antibiotic resistance [107-109] due to low concentrations of antibiotic agents in the environment is of increasing concern to scientists.

Table 2.7: Removals of some PhACs in municipal wastewater treatment works.

Compound	Reference	Raw sewage (ng/L)	Effluent (ng/L)	Removal (%)	Treatment process	Remark
Diclofenac	[104]	N/A	N/A	4	Flocculation	Lab scale
Clofibric acid		N/A	N/A	13		
Bezafibrate		N/A	N/A	None		
Ciprofloxacin	[110]	313	68	79	STP	Switzerland
Ciprofloxacin		447	62	86		
Norfloxacin		255	51	80		
Norfloxacin		435	55	87		
Iopamidol	[111]	4300	4700	None	STP	Germany
Diatrizoateb		3300	4100	None		
Ibuprofen	[112]	1000	600	52	STP	Australia, predicted by quantities of use & fugacity model
Carbamazepine		2000	1000	39		
Diclofenac		400	300	30		
Sulfamethoxazole		1000	900	27		
Naproxen		8000	4000	58		

STP: Sew treatment plant; N/A: data not available

Several studies have shown that some PhACs are not eliminated completely in the conventional sewage treatment plants and are thus discharged as contaminants into the receiving waters [101, 102, 113]. Removal of some PhACs by municipal wastewater treatment plants are listed in Table 2.7. Under effluent recharge conditions, residues of PhACs such as clofibric acid, carbamazepine, primidone or X-ray contrast agents may also leach into groundwater aquifers [114]. PhACs occurrence has been reported in ground and drinking water samples from water works using bank filtration or artificial groundwater recharge downstream from municipal wastewater treatment plants [115].

The results reported in Table 2.7 vary from zero to 87%, depending on the PhAC, the location and most likely the local treatment plant design and operating conditions including the type of biomass. While several research groups now focus on the biodegradation mechanisms of trace contaminants and the optimisation of conventional treatment processes towards the removal of such contaminants, it is unlikely that high removal of all compounds can be achieved. On the other hand, several researchers have reported almost complete removal of all PhACs using NF/RO membranes in their studies (see Table 2.8) [9, 10, 14, 44].

Table 2.8: Removal of some PhACs using NF and RO membranes.

Membrane	Compound	Feed Conc. (µg/L)	Retention (%)	Reference	Remark
XLE	Sulfamethoxazole	100	70	[10]	Lab scale
	Carbamazepine	100	91		
ESNA	Phenacetine	100	19	[9]	Lab scale
	Primidone	100	87		
	Diclofenac	100	93		
RO membrane	Carbamazepine	0.43	>99.8	[14]	Pilot scale
	Clofibric acid	0.33	>99.7		
	Diclofenac	0.329	99.7		
	Naproxen	0.038	95		
RO membrane	Clofibric acid	7.4	89	[44]	Pilot scale

Table 2.8 shows that the retention of pharmaceuticals is high in RO processes. Recent studies [9, 10, 92] show that PhACs are retained to a much higher extent than hormones despite a comparable or even lower molecular weight. This illustrates that there may be significant differences in how

these compounds are removed and such possible mechanisms will be addressed in the following section.

4. *Trace Organic Removal Mechanisms in Nanofiltration*

Following the reported variations of trace organic retention in NF (see Table 2.4, Table 2.6, and Table 2.8) in the previous section, the reasons for such variations will be explored. Hence, a more detailed discussion of trace inorganic contaminant removal in membrane filtration processes is provided. Although focusing mainly on NF, this section will go beyond the boundary of NF to include ultrafiltration (UF) and reverse osmosis (RO) membranes to a limited extent to place removal mechanisms into proper context in this often ill-defined spectrum of processes.

As NF membranes spans the gap between UF and RO membranes, while separation is thought to be accomplished via size exclusion or charge repulsion, the sorption diffusion mechanism can also contribute to the separation process [12, 15, 116]. Depending on the physicochemical characteristics of the solute and the membrane, separation can be achieved by one or several mechanisms. The word 'physicochemical' explicitly implies that separation can be due to physical selectivity (charge repulsion, size exclusion or steric hindrance) or chemical selectivity (solvation energy, hydrophobic interaction or hydrogen bonding).

Consequently, the separation process of some low molecular weight trace organics can be strongly influenced by their physicochemical interactions with the membrane polymer and/or with water. All of the mechanisms mentioned above can contribute to the separation process. These interactions are complex and the transport of organic trace organics across the membrane is an interesting topic, which to date, is not fully understood. Hence this section will provide an overview of existing parameters of importance, current mechanisms and models and their applicability to organic trace contaminant removal.

4.1 Molecular compound characteristics and groupings

Characterisation of trace contaminants is very important in understanding the fate of such compounds in the environment and to some extent in treatment systems [117]. Some generalities can be drawn by classifying organic compounds into groups based on their physical state in solution such as dispersion, aggregation and volatility [118]. In an early study, Hindin *et al.,* found that high retention was achieved for those chemical species existing primarily in the colloidal, aggregate, micelle or macromolecular form [118]. Lower retention was observed for chemical species that

exist as both an aggregate in dispersion and a discrete molecule in true solution. They also stated that volatile and low molecular weight compounds were poorly retained by the membrane. Molecular structure and conformation are also important. Reinhard *et al.,* [44] for example studied the removal of a number of trace organics that can be encountered in wastewater reclamation processes, including trihalomethanes (THMs), aromatic hydrocarbons, chlorobenzenes and benzoic acids using two pilot RO systems. Both membranes rejected branched, complex molecules but varied greatly in their retention characteristics for smaller compounds such as chlorinated solvents. They also concluded that the latter group passed through cellulose acetate membranes while being retained to some extent by polyamide membranes.

From the above it is clear that the characteristics of the contaminants are critical in the prediction of removal. While experimentation and monitoring of each contaminant of interest is not feasible, there is significant relevance in grouping contaminants into suites of similar characteristics. Besides molecular structure and electrokinetic properties, physicochemical properties especially important in understanding the separation process of trace organics in membrane nanofiltration include, but are not limited to, polarity, dissociation constant, hydrophobicity, solubility, and volatility. Details of these parameters are described below. It should be noted that values of these physicochemical parameters reported in the literature should be used with some caution, as methods and conditions used in determining them can vary widely.

Many organic molecules are electronically neutral having no net charge, neither positive nor negative. However, certain bonds in the molecule, especially bonds of the functional groups, are polar. Bond polarity results in an unsymmetrical electron distribution within the molecule. Polar organics are more reactive than non-polar ones. They may be ready to participate in chemical reactions with the membrane polymers, known as polar interactions [119]. The measure of a net molecular polarity is a quantity called the dipole moment, which is defined as the magnitude of a unit charge q times the distance r between the polar centres [119].

$$\mu = qr \qquad (2.1)$$

where q is electric charge in electrostatic units (esu), r is distance in angstroms (Å = 0.1 nm), and the dipole moment μ is a vector expressed in Debye units (D).

A number of trace organics possessing ionisable functional groups and can be ionised to become negatively charged (acid) or positively charged (base). The degree of ionisation depends on the

solution pH and the solute dissociation constant value (pK_a for acid and pK_b for base), which describes the equilibrium relationship between ionised species and non-ionised species in an aqueous system. For example, since bisphenol A (BPA) has an pK_a value of approximately 10.1, at pH above 10.1 exists mostly as negatively charged species, while at pH lower than 10.1 most BPA are neutral species. The pK_a (or pK_b) value of a compound is also related to its polarity as they both involve in the distribution of electrons within the compound.

Partitioning of trace organics to the membrane substrate or particulates and organic matter in the feed water can be understood and predicted to some degree based on the compound hydrophobicity, which is usually quantified as the relative partitioning between the liquid octanol and water (octanol-water partitioning coefficient - K_{ow}). In literature, the value of K_{ow} is commonly presented in a log scale and defined as [120]:

$$LogK_{ow} = \log \frac{C_{oc}}{C_w} \qquad (2.2)$$

where C_{oc} is the concentration of the solute in octanol and C_w is the concentration of the solute in water at equilibrium. Water solubility is defined as the maximum solute concentration in an aqueous solution at a given temperature.

The Henry constant (H) for chemical equilibrium between gaseous and aqueous phases is usually used to present the volatility of an organic compound. Similar to K_{ow}, H is a partition coefficient between water and the atmosphere:

$$H = \frac{concentration\ in\ gas\ (air)}{concentration\ in\ water} \qquad (2.3)$$

4.2 Size Exclusion

Size exclusion is a simplified retention model that is based on the physical size of a contaminant. In size exclusion, solutes larger than the pore size of the membranes are retained due to size. This is comparable to a sieving phenomenon except that in membrane filtration, pores neither have a uniform pore size nor are the solutes of a uniform size. Solutes of varying structures are not easily represented by equivalent spheres due to a difference in shapes, and molecules are flexible in size and shape as a function of stress and solution chemistry.

Several researchers consider size exclusion and sieving phenomena as having an identical retention mechanism. The process can be described using a number of simplified assumptions. It is usually

assumed that the membrane consists of a bundle of cylindrical capillaries with the pore size being the internal capillary diameter, and that solutes are spherical in shape. An average pore size and an estimated equivalent sphere diameter of solutes can be used to model the separation process. While this process is particularly useful for the retention of colloids and particulates by membranes, it can also be used for the retention of salts where the hydrated ion radius needs to be considered.

In the case of organics there is a likely deviation of shape from a sphere and molecules may also change configuration due to changes in solution chemistry or interactions with other molecules or surfaces. Retention of trace organics due to a size exclusion mechanism is illustrated in Figure 2.5.

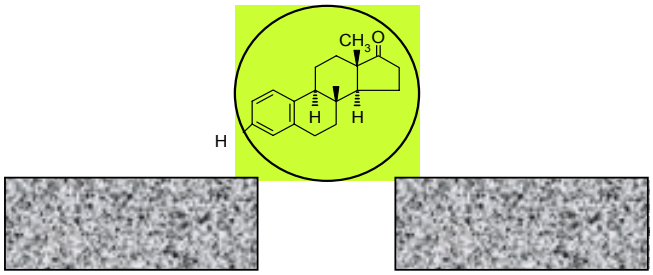


Figure 2.5: Size exclusion mechanism.

A number of models using this approach have been developed, such as the friction model and the pore model [121], to elucidate the separation process of organics using NF membranes. Having included some empirical formulae, these models are relatively simple and powerful. Prediction of solute retention can be obtained based on available physical parameters such as pore size, molecule size and pure water flux. These models have been verified using a number of non-polar neutral organics such as carbon hydrates [121, 122].

Although size exclusion is usually the prevalent retention mechanism, in many cases, the separation process is not solely based on this mechanism. Consequently, application of such size exclusion models to trace organics is limited for a number of reasons. Firstly, the presentation of organic molecules as equivalent spheres is one of the major limitations of these models. Furthermore, the geometry of organic molecules can vary significantly as a function of solution chemistry. For instance, some larger NOM molecules are known to form coils when the molecules are uncharged (at low pH) and fold out into more linear chains at high pH due to charge repulsion as described by Braghetta *et al*., and shown in Figure 2.6 [123]. Trace contaminants may also alter in conformation. More importantly they also interact with other molecules such as NOM [26, 27], which can have important implications on retention. Finally, as some trace organics can also interact with the

membrane polymer (for example via hydrogen bonding or hydrophobic interaction), which subsequently results in adsorption that is not accounted for in the steric hindrance models.

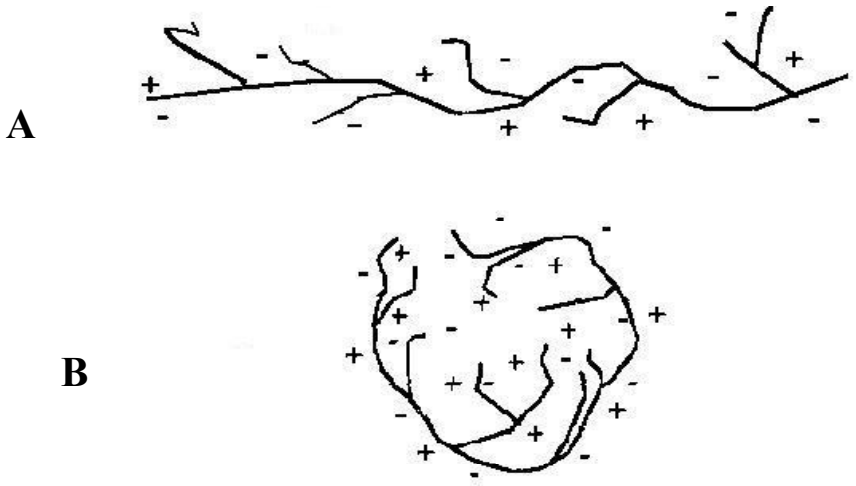


Figure 2.6: Variation of molecular dimension and shape for the example of natural organics. A: high pH, low ionic strength, low solution concentration. B: low pH, high ionic strength, and high solution concentration [123].

Adsorption of trace organic contaminants to the polymeric membranes may have a strong influence on retention. Given that surface diffusion is significantly faster than sorption diffusion, the transportation of trace organics across the membrane may be enhanced if the membrane pore is larger than the size of the trace organic. The extent of such influences on trace organic retention depends on the membrane pore size and distribution. It has been illustrated that, depending on the pore size, size exclusion, adsorption or both contribute to the retention of the trace organic estrone [124].

There are several models relating molecular weight and size of contaminants. Molecular weight is the most easily accessible parameter that indicates the size of a molecule. Many studies have subsequently focused on molecular weight to obtain information about retention of neutral organics by NF. The molecular weight cut-off (MWCO), which is the molecular weight of a solute that corresponds to a retention of 90% [125], is commonly used by most membrane manufacturers as a measure of the retention properties of NF membranes.

However, molecular weight cut-off does not provide information on the retention of organics having a molecular weight smaller than the MWCO [126]. In addition, as dimensional parameters

of the molecule are not taken into account, retention of organics with a similar molecular weight but different molecular structure may differ. It is hence desirable to be able to use a structural parameter to estimate retention. Consequently, the Stokes radius is often regarded as a better parameter to describe molecule size, when the molecule is assumed to be spherical in shape. The Stokes-Einstein radius of a molecule is defined as [127]:

$$r_s = \frac{kT}{6\pi\eta D_s} \qquad (2.4)$$

where k is the Boltzmann constant (J/mol.K), η is viscosity (kg/m.s), T is temperature (K) and D_s is diffusion coefficient (m^2/s).

As the equation indicates, the Stokes radius is essentially related to the diffusion coefficient, which is not available for many organics. Fortunately, the diffusion coefficient can be estimated from molecular weight using several different methods as summarised in Table 2.9. However, the variation between different methods can be up to about 125% [128].

Table 2.9: Summary of methods to estimate diffusion coefficients [128].

Method	Equation	
Wilke-Chang	$D_s = 1.193 \cdot 10^{-7} \frac{M_s^{1/2} T}{\eta \cdot V_s^{0.6}}$	(2.5)
Worch	$D_s = 3.595 \cdot 10^{-14} \frac{T}{\eta \cdot M^{0.53}}$	(2.6)
Tyn-Calus	$D_s = 8.93 \cdot 10^{-8} \frac{V_w^{0.267} T}{V_s^{0.433} \eta} \left(\frac{\sigma_w}{\sigma_s} \right)^{0.15}$	(2.7)
Scheibel	$D_s = 8.2 \cdot 10^{-8} \left(1 + \left(\frac{3V_w}{V_s} \right)^{2/3} \right) \frac{T}{\eta V_s^{1/3}}$	(2.8)

Some size parameters other than Stokes radius worth mentioning include the equivalent molar diameter [126] where the molecule is also assumed to be spherical, and STERIMOL parameters [69] where both molecular width and length are calculated taking into account Val der Waals effects. However, there is usually a good correlation between these parameters and the Stokes radius [126].

An organic molecule can also be presented as a cylinder whose height and diameter are determined following an energetic optimization procedure, which can be carried out using a computer program such as HyperChem [126].

Further studies are essential to take into account such influences on trace organics retention with a rigorous approach coupled with grouping of contaminant characteristics. While size is an important factor, the impact on retention is also influenced by the charge of the molecules that may enhance attraction or repulsion from the membrane.

4.3 Charge Interaction between ionic species and NF/RO membranes

Wang *et al*., [129] have proposed a model to describe the transport of an organic electrolyte across a NF membrane by combining the space-charge and steric-hindrance pore physical phenomena. The model was consequently named the electrostatic and steric-hindrance (ES) model. It indicates that both electrostatic and steric-hindrance can contribute to the retention of organic electrolytes by NF membranes. Based on this model, solute retention is a function of the ratio of charge density of the membrane to ionic concentration, solute radius to pore radius of the membrane, and the relative mobility between cations and organic anions. As a result, one would expect that retention of these trace organics could be influenced by solution chemistry such as pH and ionic strength. Braghetta [130] has illustrated schematically the effect of solution pH and ionic strength on the "apparent" pore size of the membrane as in Figure 2.7. Such variation of membrane structure as a function of solution chemistry usually manifests itself with a variation of flux and salt retention.

Some trace organics can possess a negative or positive charge when the molecules dissociate at high or low pH. For example, p-aminobenzoic acid has a negative charge at pH higher than 4.8 (pK_a of carboxyl group) while it has a positive charge at lower pH (amine pK_a = 4.6). Negatively charged organics often experience higher retention than uncharged organics with the same size, which can be attributed to electrostatic repulsion between the molecules and the negative functional groups of the membrane. On the other hand, positively charged organics are poorly retained by the negative membranes. Berg *et al*. [65] reported a significant increase in retention of the negatively charged organic, mecoprop, by five different negatively charged membranes at high pH. Williams *et al*. [131] also showed that the retention of p-aminobenzoic by negatively charged membranes resembles its speciation as a function of pH with an increase of retention as charge repulsion increases (see Figure 2.8). Although electrostatic interaction dominates the separation process, steric hindrance also appears to influence the retention of such solutes [65].

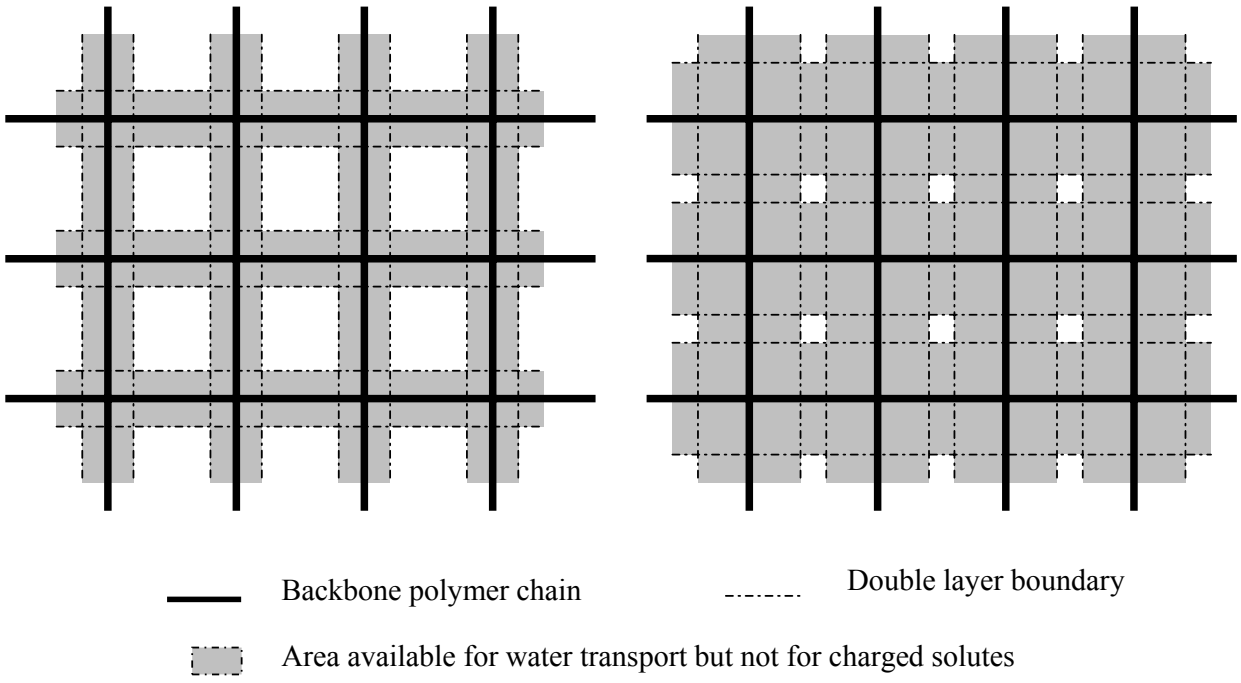


Figure 2.7: Schematic effect of solution pH and ionic strength on membrane properties. Left: low pH and low ionic strength. Right: high pH and high ionic strength (adapted from Braghetta [130]).

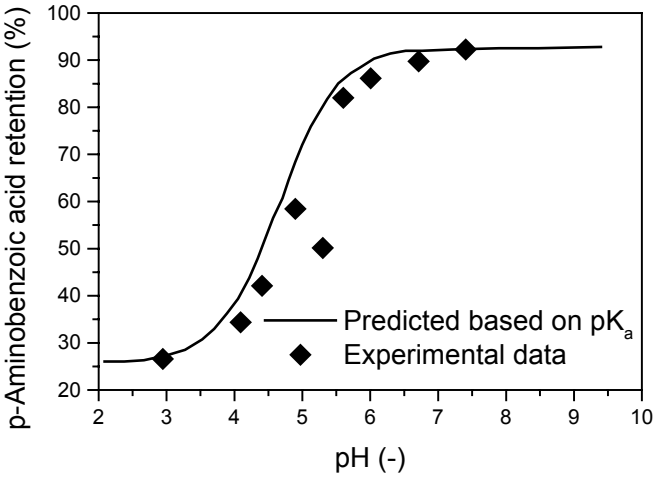


Figure 2.8: *Effect of pH on retention of p-aminobenzoic acid by a negatively charged NF membrane (adapted from [131]).*

The pH value of the feed solution can also affect characteristics of the membrane; hence, their retention properties. Most significant is the membrane surface potential, which is often measured as zeta potential. Figure 2.9 shows the surface zeta potential of several NF membranes as an example. In general, zeta potential of the membrane surface can change from a positive to a negative value as the solution pH increases. Subsequently, electrostatic interaction between an ionic compound and the membrane surface can also vary according to the solution pH. Bellona and Drewes [132]

reported a strong pH dependence of retention of several organic acids, which closely resembles the speciation of such compounds as a function of pH.

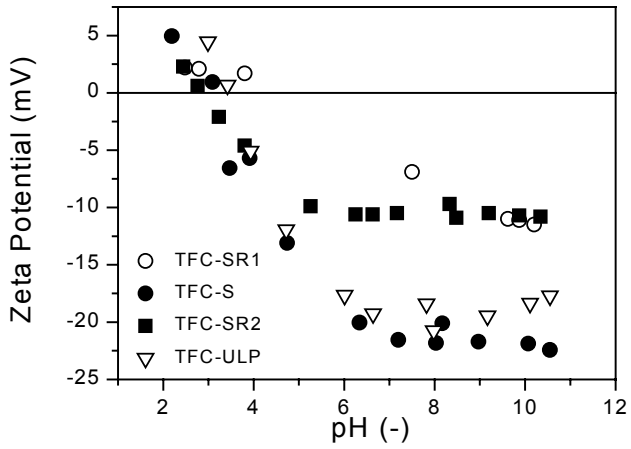


Figure 2.9: *Surface zeta potential of several NF/RO membranes as a function of pH (adapted from [124]).*

In addition to the change in zeta potential of the membrane surface, Childress and Elimelech [133] have also illustrated the dependence of membrane pore size on the pH of the feed solution using polyamide NF membranes. At high or low pH, functional groups of the membrane polymer can dissociate and take on positive or negative charge fractions. Repulsion between these fractions in the membrane polymer reduces or "closes up" the membrane pores. At the pore surface point of zero charge (or the isoelectric point), membrane functional groups are minimal in charge and hence the pores open up, as the absence of repulsion force contributes to the widening of the membrane pores. This was confirmed experimentally when a drop in salt retention (corresponding to a peak in permeate flux) at this pH compared to low or high pH was observed [133]. On the other hand, Braghetta reported a decrease in retention due to charge repulsion between the polymer chains, and hence increased pore size [123]. However, this phenomenon in trace organic retention has yet to be examined and one would expect that the effects of pH on trace organic characteristics and membrane pore size cannot be easily separated.

4.4 Interactions due to polarity

Separation of polar organics by a NF membrane is, in general, even more complex as the process is not only governed by charge repulsion and size exclusion but is also influenced by other physicochemical interactions between solutes and the membrane polymer. These polar interactions can influence the partitioning of solute between bulk solution and the membrane pores, sorption of solute into the water-membrane interface and even sorption of solutes into the membrane polymer.

Van der Bruggen *et al.,* have successfully combined size exclusion and polarity effects to explain the retention of four pesticides [68]. Consequently, the polarities of both trace organics and the membrane polymers are of importance in predicting the retention of a trace organic. In addition, it is necessary to identify chemical parameters that contribute to the polarity of trace organics.

While the dipole moment can be experimentally determined, it is not practical to measure dipole moments of all trace organics, given the large number of contaminants that exist. Sourirajan and Matsuura [116] have identified a number of parameters indirectly related to the polarity in their magnificent work in the early 1970s. The main quantifiable parameters related to polarity are:

- Hydrogen bonding ability of the solute as represented by its $\Delta\nu_s$ (acidity) relative shift in the OH band maximum in the IR spectra of the solute in CCl_4 and ether solutions),
- Taft (δ^* or $\Sigma\delta^*$) or Hammett (δ or $\Sigma\delta$) numbers for the substituted group in the solute molecule with reference to a given functional group,
- pK_a value of solute.

While the pK_a value is commonly reported in literature, the use of hydrogen bonding ability and Taft (or Hammett) number is limited due to their complexity and unavailability.

In addition to these indirect polarity parameters, several researchers have attempted to relate retention and log K_{ow} (logarithm of the n-octanol/water partition coefficient) or hydrophobicity of the membrane surface in examining the separation process of trace organics [69, 134-136]. Nevertheless, none of them have conclusively reported any characteristic correlations. Note that some researchers refer to this parameter as log P. In fact, log P and log K_{ow} are identical. Since log K_{ow} is an indirect measure of the molecule polarity, it is uniquely related to the compound polarity parameters [116].

Similar to the dipole moment, data on the values of these parameters are not available in the literature for many trace organics. Comparison between organics of similar structure but different in functional groups or vice versa can be made given the hydrocarbon skeleton and composition of the compounds. Based on a reference organic, the chemical characteristics of other organics can be qualitatively and quantitatively predicted. For example, a method to estimate the pK_a value of an organic based on the pK_a value of other organics similar in structure has been described by Perrin [137]. Several commercial computer software packages such as HyperChem and Pallas have been developed to predict these parameters. However, when using such software, one should be cautious

that the database of referenced structures can be limited and they may fail to give a close estimation in some situations.

Seeing the difficulty in quantifying the chemical characteristics of some contaminants, the relationships between chemical characteristics such as polarity and NF retention remain unavailable. Consequently, there are no universal indicators for the retention of such polar trace organics using NF. Membrane supplier information such as molecular weight cut-off (MWCO) and salt retention are clearly not appropriate as salt retention often fails to serve as an indicator for trace organics removal [134] and MWCO should only be applied to non-polar neutral organics with caution as discussed earlier. It is hence not surprising that Kiso *et al.,* [69] showed a poor correlation between the retention and molecular weight of 11 different aromatic pesticides as illustrated in Figure 2.10.

Sourirajan and Matsuura [116] examined the relevance of these polarity parameters as described earlier to retention, using 65 organic compounds with different functional groups. Experimental results showed that there is a unique correlation between $\Delta\nu_s$ (acidity) and retention of monohydric alcohols and phenols, which exist essentially as unionized molecules in aqueous solutions. Similarly, an excellent correlation has been found between the Taft number ($\Sigma\delta^*$) and the retention of mono and polyhydric alcohols.

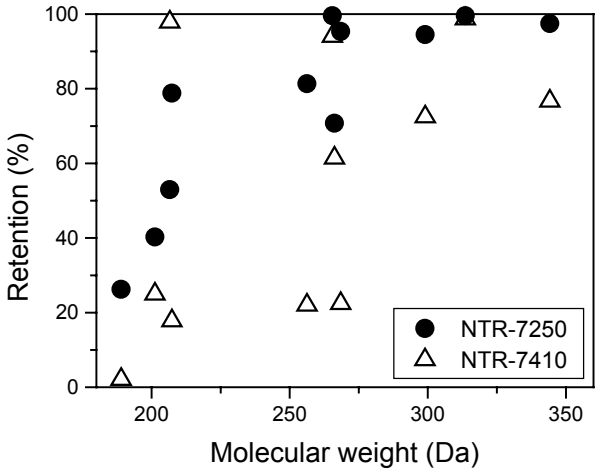


Figure 2.10: Retention of 11 aromatic pesticides by NF membranes as a function of molecular weight (adapted from [69]).

Sourirajan and Matsuura subsequently explained these correlations using a sorption-capillary flow mechanism; where the sorption of solute with higher polarity to the membrane-water interface is

favourable, solute transport across the membrane is enhanced, hence decreasing retention [116]. These results establish the relevance of polar parameters to retention of these alcohols and phenols. More importantly, Sourirajan and Matsuura reported that while retention is positive for solutes whose acidities (or Taft numbers) are less than that of water $\Delta\nu_s$ (acidity of water) = 250 cm^{-1} ($\Sigma\delta^*$=0.49), retention can be negative, zero or positive for those solutes (such as phenols) whose acidities or Taft numbers are higher than that of water, depending on filtration conditions. Sourirajan and Matsuura have illustrated this finding using phenol and p-chloro-phenol and several different membranes [116]. In general, for such solutes retention decreases as the driving force transmembrane pressure increases. This separation phenomenon is distinctive for polar organics as it is in fact in contrast with the separation process of other solutes such as colloids, salts and neutral non-polar organics.

While polarity is an important factor, again it is not the only factor influencing the separation process. Different correlation curves obtained between retention of ethers, ketones, aldehydes, esters and alcohols, plus their acidities and Taft numbers [116], clearly indicate that factors other than polarity can also influence the separation process. Identifying and including all of these factors in a mechanistic model to understand and predict retention of trace contaminants would be a complicated task and one that much more dedicated efforts should be devoted to in future research.

4.5 Adsorption

Adsorption (or partition) of trace organics to membrane materials is an important aspect of trace organic removal using NF. Several researchers have observed significant adsorption of some trace organics into the membrane polymer [8, 9, 43, 45, 69, 131]. In fact, adsorption is recognized as the first step in the transport mechanism of water and in some cases solutes across the membrane in the well-known sorption-diffusion model [131, 138]. Trace organics, which can adsorb to the membrane, usually have high log K_{ow} or hydrogen bonding capacity and are sparely soluble in water.

According to the sorption-diffusion model, water flux across the membrane is thought to be greatly dependent on its ability to form hydrogen bonds with the hydrophilic groups of the membrane polymer, while specific adsorption due to hydrogen bonding can reduce water permeation. Possible formation of hydrogen bonding between the membrane polymer and a trace organic is illustrated in Figure 2.11. This indicates the likelihood of hydrogen bonding playing a major role in retention by NF. This premise is supported by an earlier study, in which Williams *et al*., [131] reported

significant adsorption of benzene with no hydrogen bonding capacity but negligible water flux drop. On the other hand, there was a 60% drop in flux due to adsorption of 2,4-dinitrophenol, a compound with a high hydrogen bonding capacity, to an aromatic polyamide membrane. This can be attributed to the competition between 2,4-dinitrophenol and water for hydrogen bonding sites. Adsorption can also be accomplished via hydrophobic interaction. Kiso *et al*., besides showing a poor correlation between molecular weight and retention (Figure 2.10) also investigated the relationship between log K_{ow} versus retention and adsorption of eleven aromatic pesticides using NF membranes [69]. While there was no significant correlation between retention of these pesticides and log K_{ow}, there was a good correlation between adsorption of these pesticides and log K_{ow}. Hydrogen bonding and hydrophobic interaction can act independently or together. In the later case, it is often difficult to separate the effect between them.

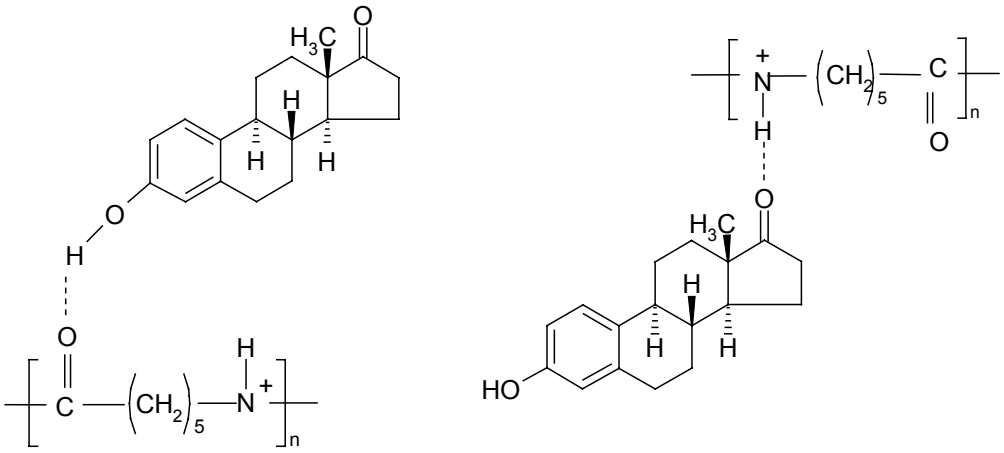


Figure 2.11*:* Hydrogen bonding between membrane polymer (polyamide) and natural hormones estrone.

Adsorption of trace organics to the membrane has two important implications. Firstly, it may result in the accumulation of trace organics, which can lead to several deteriorative problems. Secondly, concentration gradient built-up as a result of adsorption (or partition) followed by diffusion can possibly reduce the membrane effectiveness to some extent.

Trace organics can accumulate in the membrane to a considerable degree and changes in operation conditions may be able to cause a shift in adsorption/desorption equilibrium, and subsequently release some of the accumulated contaminants [139]. For example, the concern of estradiol release during membrane cleaning has been raised, where alkaline solutions at pH 11 are commonly applied [140]. At this pH, estradiol dissociates and becomes negatively charged. Subsequently,

desorption of estradiol occurs due to charge repulsion between the negatively charged estradiol and the negatively charged membrane surface.

The transport of adsorptive trace organics in the membrane polymer can be explained by the sorption-diffusion model, where solutes adsorb (or partition) into the membrane and are transported across the membrane by diffusion. Adsorption itself occurs due to hydrophobic interaction or the formation of hydrogen bonding between the membrane polymer and trace organics. Diffusion in the dense polymeric phase can possibly be accomplished by a series of successive jumps from one equilibrium position to another, which usually involves the formation and breakage of secondary bonds [141]. Such "make-and-break" action can be the result of switching between two bonding sites or between a hydrophobic bond to a substrate and a hydrogen bond to water [142, 143]. It has been previously observed that compounds with hydrogen bonding capacity are usually retained less [138]. Several researchers have used the term "solute membrane affinity" to cautiously refer to this phenomenon [9, 134].

5. *Conclusions*

This chapter describes the relevance of NF/RO membrane filtration as a notable approach to remove trace contaminants, both organic and inorganic, in aquatic environments. A variety of trace contaminants, their occurrences in various water bodies, their health effects, and the perspective in their removal by NF/RO membranes have been summarised. Some insights into retention mechanisms have also been discussed.

Retention is generally governed by three factors including steric hindrance, electrostatic interaction, and physicochemical interactions such as solute membrane affinity and polarity. While the first two factors often dominate the separation process, the latter factors play a subtle but no less critical role. All of these factors depend strongly on the physicochemical characteristics of the solute, which may be influenced by its environment. Since trace contaminants often exhibit distinct physical and chemical characteristics, the retention of trace contaminants in nanofiltration (as in other processes) can be very compound specific.

An attempt to fully document research work relevant to trace contaminant removal in nanofiltration has been made. However, the variety of operational parameters used in those studies has rendered a clear and conclusive interpretation to a limited extent only. The chapter illustrates the influence of many inter-dependent factors on trace contaminants retention in seemingly simple nanofiltration

processes. Much more dedicated work is needed to fully appreciate the complexity of trace contaminant separation processes in nanofiltration and to allow the development of adequate predictive models. The discussion presented here places a particular emphasis on both physical and chemical properties of trace contaminants, and their interactions with the membrane polymer and other entities in the solution. The literature review presented here indicates a clear limitation of the current understanding of the removal mechanisms as well as the physicochemical interaction influence on the separation of trace organics using NF/RO membrane filtration processes. There is a lack of critical delineation amongst trace organic retention and their physicochemical properties as well as the membrane characteristics.

Trace contaminant removal is an important feature of nanofiltration and reverse osmosis processes. It is this characteristic that has driven nanofiltration into the water market and will continue to do so with an increased emphasis on trace contaminant regulation. A thorough understanding of mechanisms will assist the development of membranes that are able to remove targeted compounds at higher and higher efficiency. The author and other membrane researchers are looking forward to watching and contributing to this progress.

Chapter 3

Materials and Methods

1. *Introduction*

As previously delineated in Chapter 2, NF/RO membrane filtration processes of trace organic contaminants are subjected to the influence of many inter-dependent factors. In order to fully appreciate the complexity of trace contaminant separation processes in nanofiltration and to allow the development of adequate predictive models, it is critical to characterize both the membranes and the trace organic contaminants in great detail. Information about their physicochemical properties can then be considered to elucidate the separation phenomena observed during filtration experiments.

In this chapter, physicochemical properties of the selected membranes and trace contaminants were meticulously examined. Data were obtained from laboratory measurement, literature research, and/or computer simulation. Solution preparation, the chemicals used, and their origins were described in detail. An overview of the experimental systems and associated protocols as well as the analytical techniques used in this study was also included.

2. *NF/RO Membranes*

2.1 Selected membranes & their characteristics

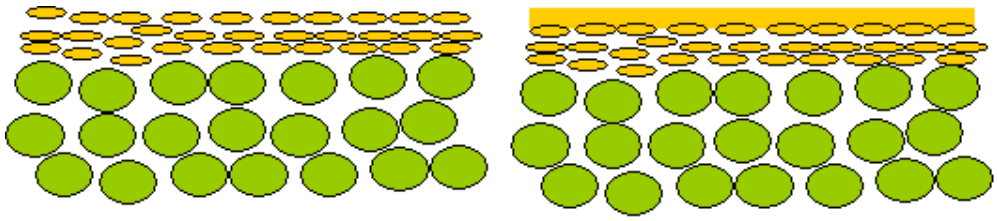
Ten commercially available NF/RO membranes from three manufacturers were selected for this study. They span a wide spectrum from a relatively low NaCl retention NF membrane (i.e. the TFC-SR2) to an almost complete NaCl retention RO membrane (i.e. X-20) (see section 2.6). Their names, manufacturers, and polymeric materials are listed in Table 3.1. Although polymeric make-ups of the membranes are given (see Table 3.1), the exact composition is unknown. Furthermore, as all membranes have similar (or almost the same) polymeric make-ups, little information about the membrane properties can be obtained without detailed membrane characterisations. In this chapter, properties of the selected membranes are discussed. The membranes are characterised in surface morphology, surface charge, hydrophobicity, pure water flux and salt retention.

Table 3.1: Membrane material as indicated by the manufacturers.

Membrane	Type of membrane	Manufacturer	Membrane material
TFC-ULP	NF/RO	Koch membrane	Polyamide on Polysulfone support
TFC-S	NF		
TFC-SR1	NF		
TFC-SR2	NF		
X-20	RO	Trisep	Polyamide-urea Composite
ACM-4	RO		
XN-40	NF		
TS-80	RO		
NF 90	NF	FilmTec Corp	Polyamide layer on polysulfone support with a semi-aromatic piperazine based
NF 270	NF		

2.2 Membrane skin layer thickness

The development of anisotropic membranes has led to a major breakthrough in membrane technology. These anisotropic membranes consist of a very thin top layer called the skin, and a supporting layer that is much thicker and more porous. The skin layer provides selective properties to the membrane. Permeate flux is inversely proportional to the membrane skin layer thickness. The supporting layer possesses negligible resistance to water flux or solute selectivity. Its main purpose is to provide mechanical support for the skin layer. Most NF/RO membranes are anisotropic, and they can be categorised into two types: asymmetrical and thin film composite (Figure 3.1). If the membrane is prepared from the same material, it is called asymmetric. On the other hand, thin film composite membranes consist of more than one polymer layer and originate from different materials. All membranes selected for this study are thin film composite.



Asymmetric Thin film composite

Figure 3.1: Asymmetrical versus thin film composite membranes (Drawing is not to scale).

The skin layer has the main functions of the membranes as both water flux and selectivity depend mostly on its structure and thickness. Skin layer thickness of most RO membranes ranges from 300 to 500 nm, roughly less than 1 percent of the supporting layer thickness. Such figures are often reported based on indirect measurement methods or theoretic calculations. Direct measurement of

these very thin layers was extremely difficult. Freger and his co-workers have reached a major breakthrough and clearly shown the skin layer - supporting layer interface in a high resolution transmission electron microscopic (TEM) picture (see Figure 3.2) [144, 145]. They suggest that NF membranes have much thinner skin layer, in the range of 15 nm to less than 100 nm [144, 145]. This is probably the case for the so-called low-pressure RO membranes. Reducing the membrane skin layer thickness results in higher water flux, but can also have important implications on the retention of contaminants. In particular, it may lessen the retention of certain trace contaminants, as will be discussed in subsequent chapters.

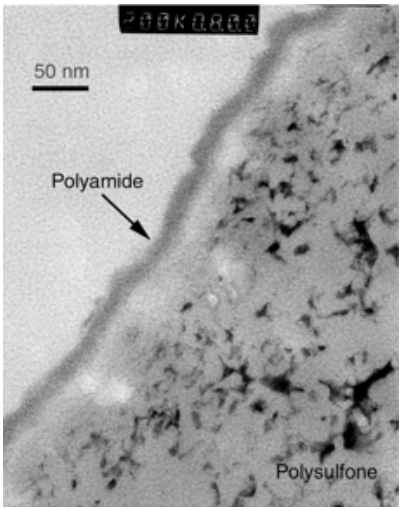


Figure 3.2: Cross sectional image of an NF membrane taken by a TEM showing the active polyamide skin layer on top of the porous polysulphone supporting layer. Skin layer is approximately 15 nm in thickness. The membrane was stained with uranyl nitrate. (Source: adapted from [145].)

2.3 Membrane morphology

An Atomic Force Microscope (AFM) is an excellent tool to study the topography of the membrane skin layer. An AFM consists of an extremely sharp tip mounted to the end of a tiny cantilever spring, which is moved by a mechanical scanner over the surface to be observed. Every variation of the surface height varies the force acting on the tip and therefore varies the bending of the cantilever. This bending is measured and recorded line by line. The image is then reconstructed by computer software associated with the AFM.

Surface morphology of the membranes was characterised using a Digital Instrument Nanoscope with a Nanoscope V controller (Vecco USA). The AFM was used in a contact mode with standard contact mode tips (Olympus). Images were scanned at a rate of 1 Hz. Scanning size was 2 μm by 2 μm. Ambient conditions were maintained at approximately 20 °C and 30 % relative humidity. AFM

images of Trisep, Koch, and Filmtec membranes are shown in Figure 3.3, Figure 3.4, and Figure 3.5, respectively.

The surface of X-20, TS-80, ACM-4, and TFC-ULP membranes shows a typical nodular (hills and valleys) morphology (see Figure 3.3 and Figure 3.5). This is typical for most RO membranes as also observed by other researchers [144, 146, 147]. A similar pattern can be seen for other NF membranes under study (see Figure 3.3 to Figure 3.5) with the hill to hill distance being much smaller, which correlates well with the much lower thickness of the active later (15–40 nm for NF against 200–300 nm for RO). This morphology seems to be influenced by the underlying supporting layer, and may be viewed as a fingerprint of the TFC polyamide composites [144].

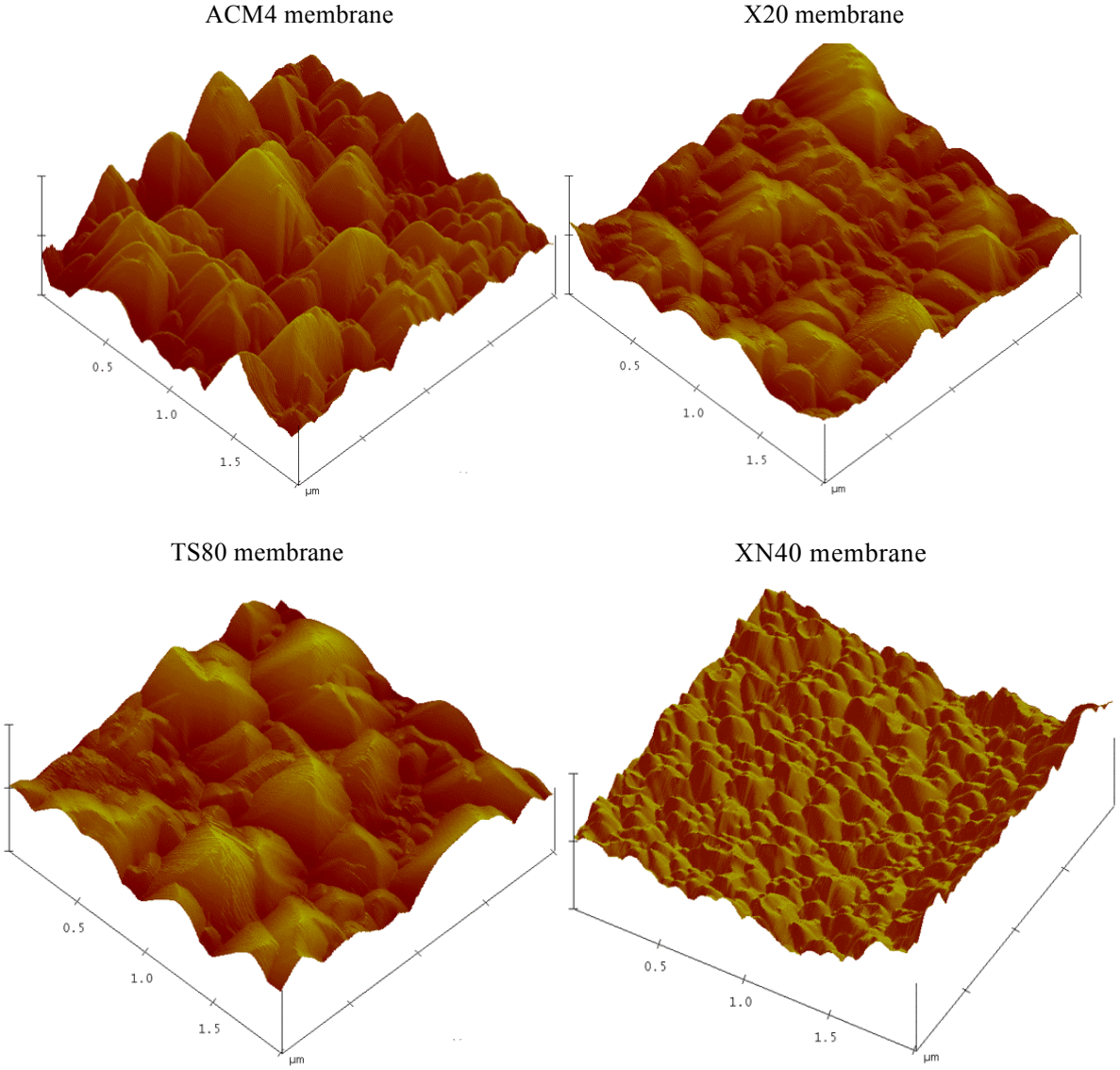


Figure 3.3: Surface topography image of 4 Trisep membranes (ACM4, X20, TS 80, and XN 40).

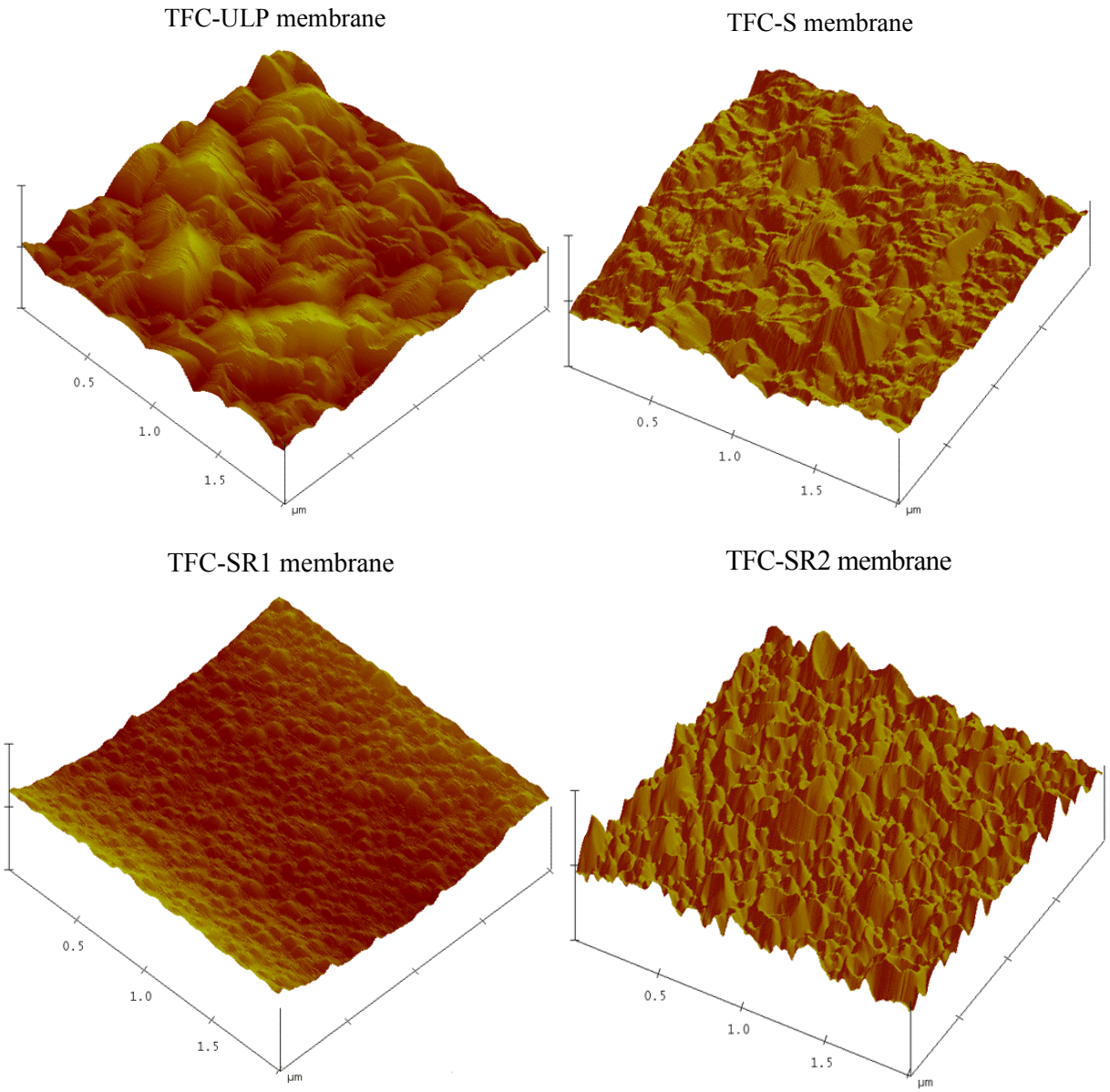


Figure 3.4: Surface topography image of 4 Koch membranes (TFC-ULP, TFC-S, TFC-SR1, and TFC-SR2).

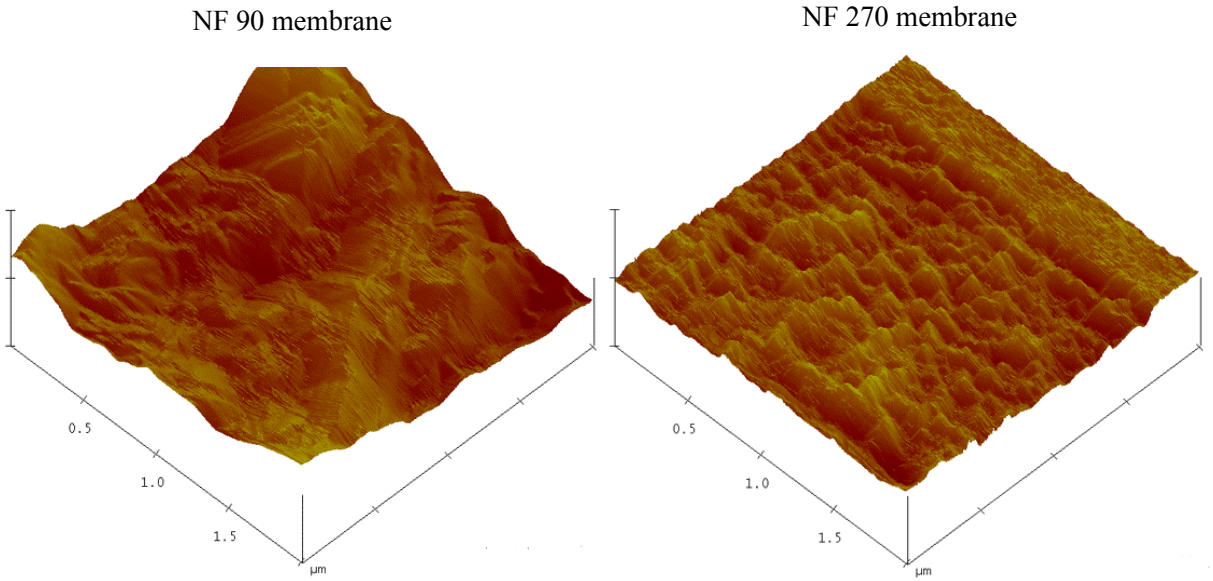


Figure 3.5: Surface topography image of 2 Filmtec membranes (NF 90 and NF 270).

Hill to hill distance of high pure water flux membranes (XN-40, TFC-SR2, TFC-S, and NF-270) is much smaller than the others. Interestingly, volcanic pattern is obvious for XN-40 and TFC-SR2, the two most porous membranes in this study. While AFM can be used to measure pore size and pore size distribution of some MF and UF membranes [148-152], many maintain their reservation when using AFM to characterise NF membrane pore size. Despite the fact that "pore structure" of the TFC-SR2 membrane AFM image is quite clear (see Figure 3.4), it probably represents the underlying supporting layer morphology rather than actual pores of the membrane. It is important to recall that the skin layer thickness in this case can be as thin as 15 nm, much smaller than the features visible in Figure 3.4. Later pore size characterisation studies indicate that the pore size of this membrane is indeed less than 2 nm in diameter and hence not visible with AFM examination.

The membrane surface roughness is usually directly linked to its fouling potential and rough membranes are often more prone to fouling than smooth ones [147]. Rough membranes may also possess more available surface for adsorption than smooth membranes. As can be seen in Figure 3.3 and Figure 3.4, XN-40 and TFC-SR2 are much rougher than their counterparts from the same manufacturer.

A scanning electron microscopic technique was also used to further characterize the surface morphology of membrane surface. Membrane samples were sputtered with an extremely thin layer of Chromium. Images of the membranes were then taken using a Hitachi S900 – Field emission

Electron Microscope. SEM images are presented in Figure 3.6, Figure 3.7, and Figure 3.8, for Trisep, Koch, and Filmtec membranes respectively.

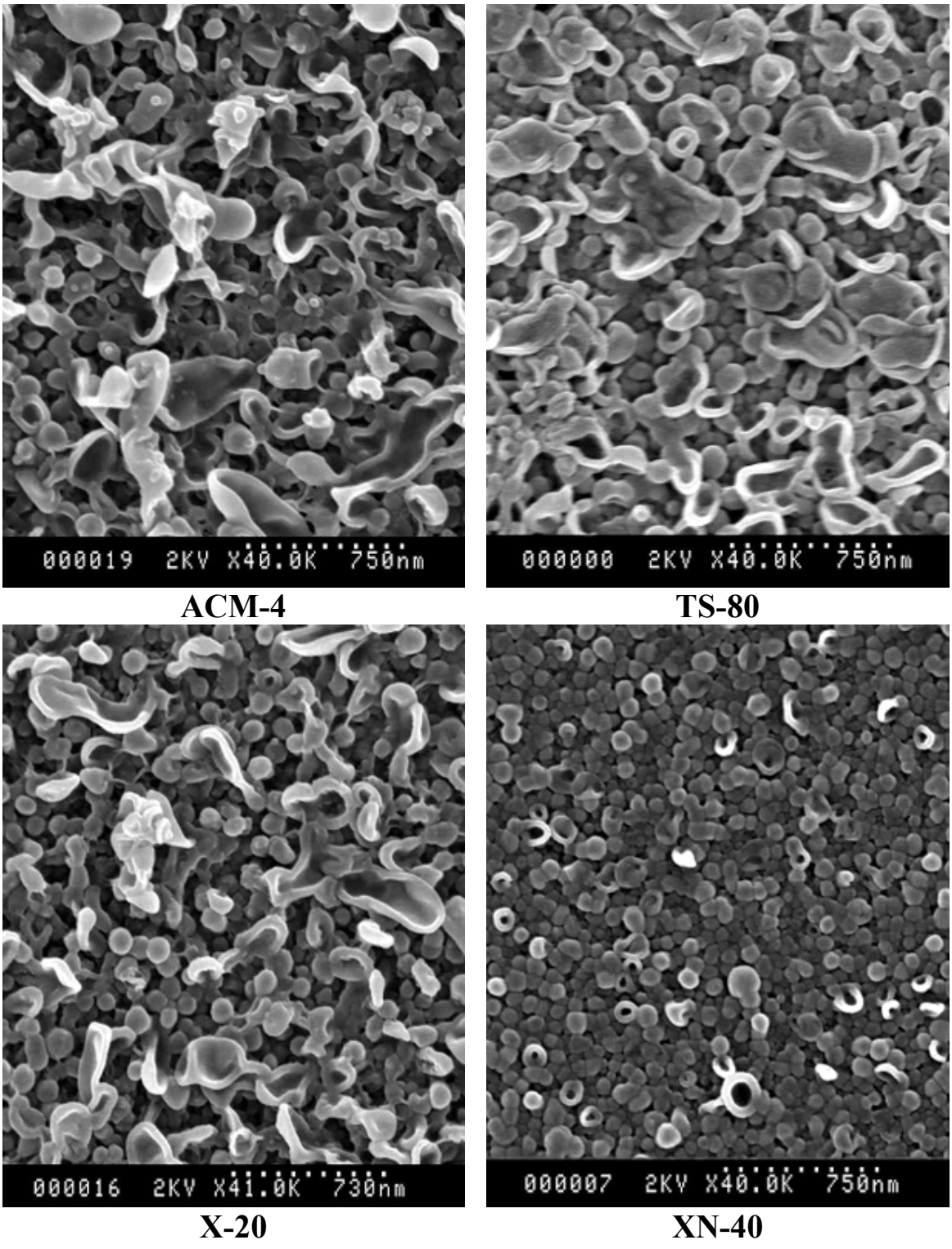


Figure 3.6: SEM image of 4 Trisep membranes (ACM4, X20, TS 80, and XN 40).

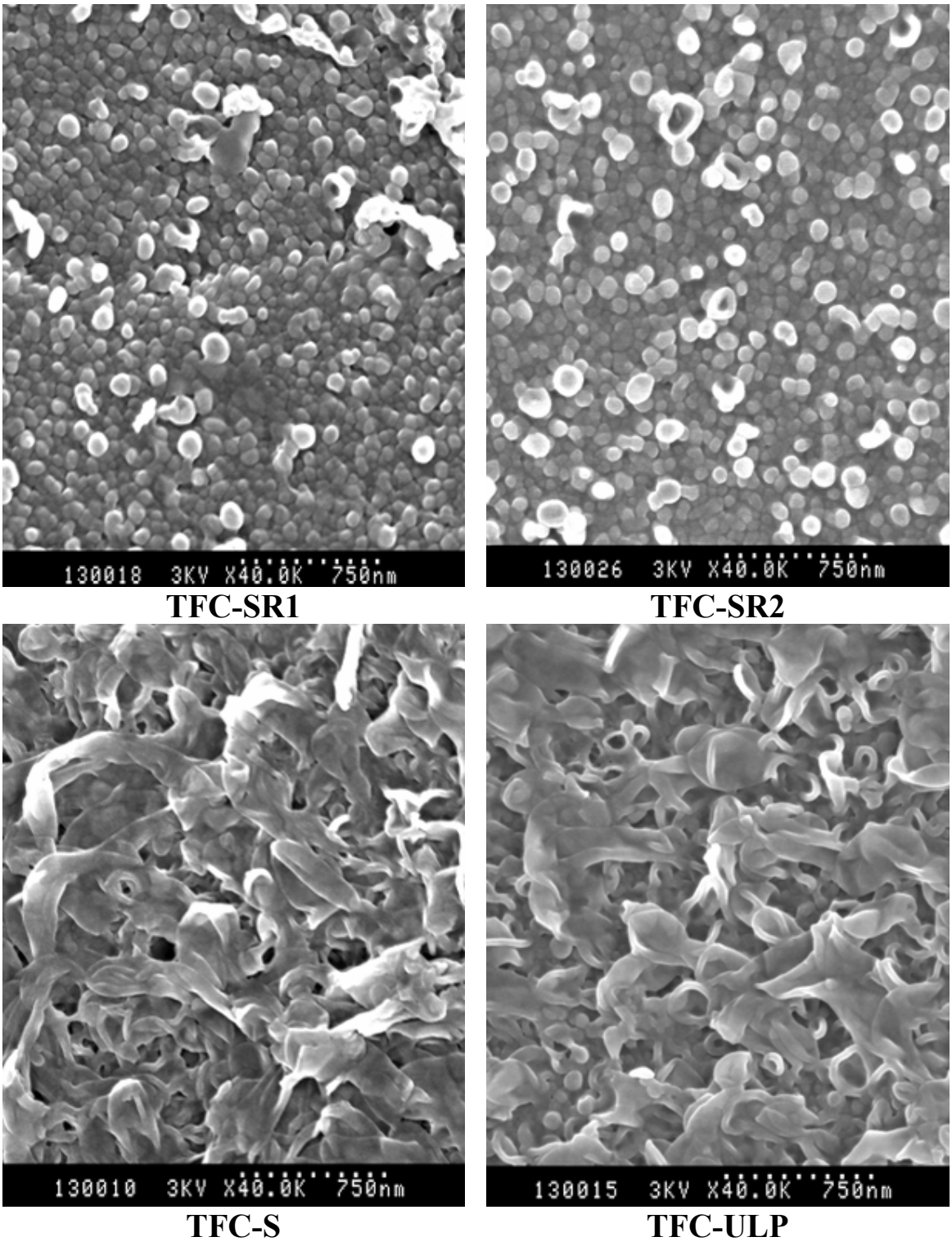


Figure 3.7: SEM image of 4 Koch membranes (TFC-ULP, TFC-S, TFC-SR1, and TFC-SR2).

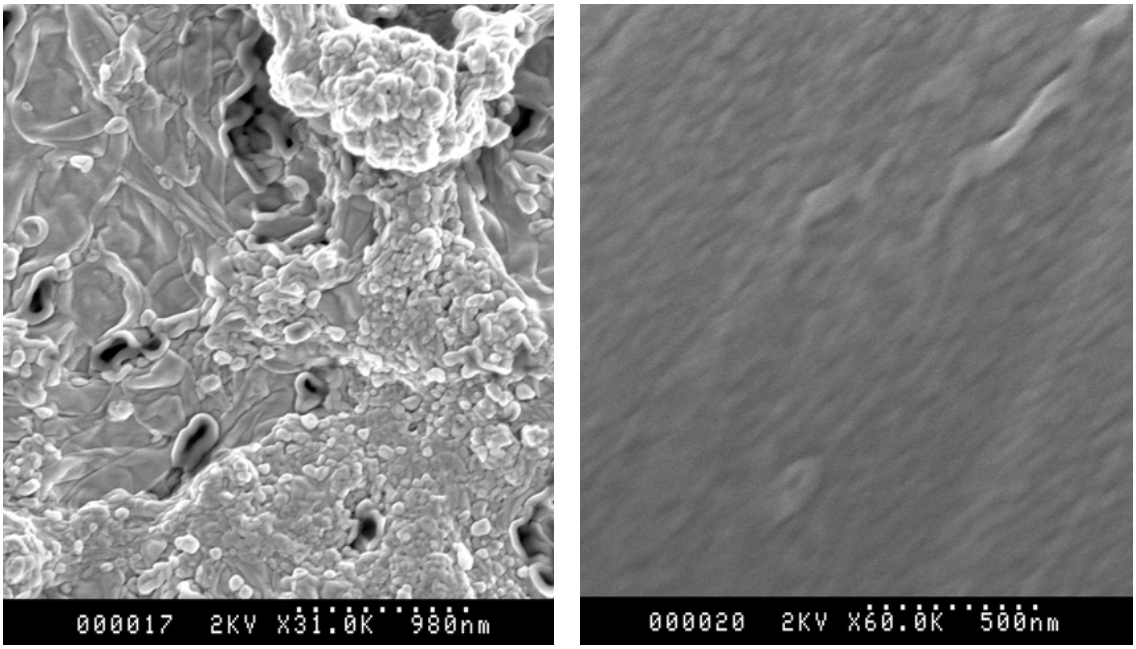


Figure 3.8: SEM image of 2 Filmtec membranes (NF 90 and NF 270).

SEM images of these membranes are strikingly different from that obtained by the AFM. However, this is not surprising as SEM images that often complement AFM images are unsuitable when the skin of the membranes is so thin that the "polysulfone background in the SEM images largely overwhelms it" as previously observed by Freger *et al.* [144]. This once again highlights the extreme small thickness of the membranes selected in this study. It is possible that SEM pictures in this case present the underlying supporting layer morphology rather than the membrane's actual active surface.

2.4 Membrane surface charge

Surface charge of the membranes plays a critical role in solute retention. In fact, charge repulsion is one of the major retention mechanisms of NF and RO membranes [16, 133, 153, 154]. Membrane surface charge can be obtained by zeta potential measurement. The zeta measurement technique and principle were described in detail by Elimelech and his co-workers [155, 156]. Zeta potential of the membranes selected for this study was measured as a function of the solution pH using a Brookhaven Instruments Corp. (Holtsville, NY, USA) BI-EKA instrument. This instrument has a cross-flow slit geometry. The results are shown in Figure 3.9 and Figure 3.10 for the 10 membranes selected in this study.

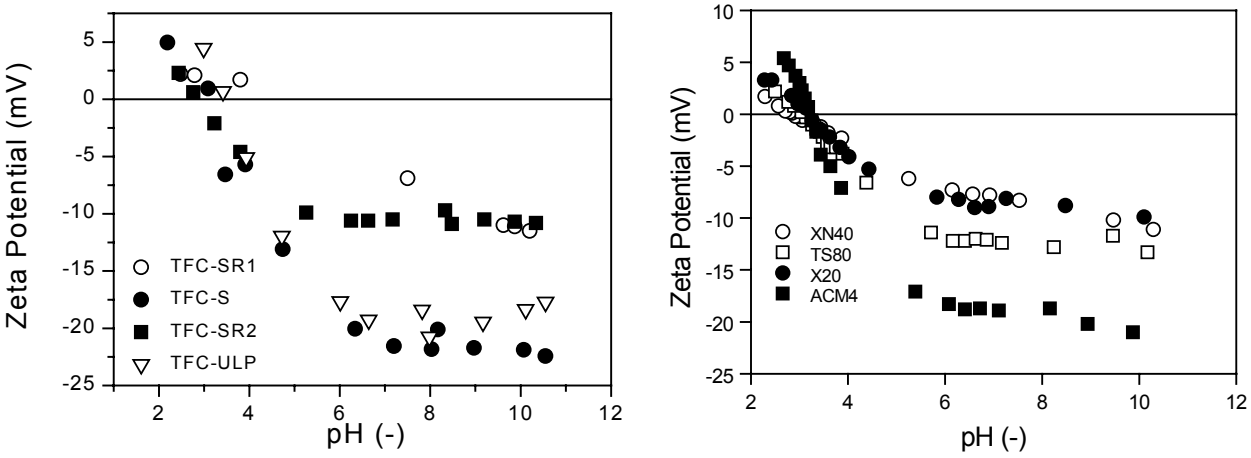


Figure 3.9: Zeta potential of 4 TRisep membranes (ACM-4, TS-80, X-20, and XN-40) and 4 Koch membranes (TFC-SR1, TFC-SR2, TFC-S, and TFC-ULP). Measured in background solution containing 10 mM NaCl and 1 mM $NaHCO_3$.

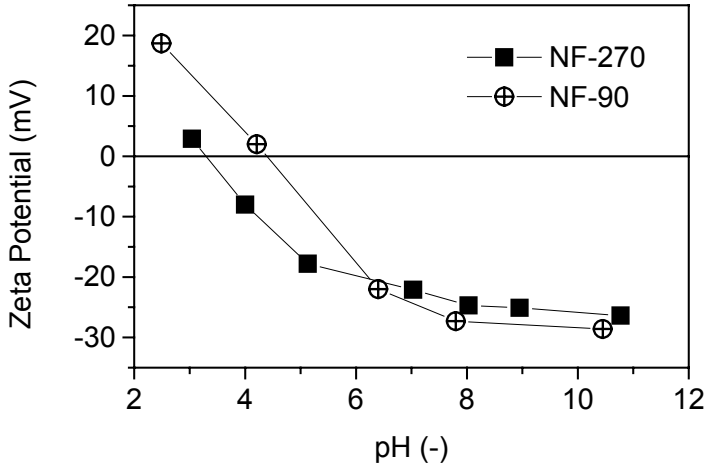


Figure 3.10: Zeta potential of 2 Filmtec membranes (NF-270 and NF-90). Measured in background solution containing 10 mM NaCl and 1 mM $NaHCO_3$.

As can be seen in Figure 3.9 and Figure 3.10, the membrane isoelectrical points are around pH 4. Above this pH, the membrane surface is negatively charged, while below this pH it is positively charged. This variation in pH is due to the dissociation of the membrane functional groups (such as carboxylic and amide functional groups), and depending on the solution, pH can carry a fixed negative or positive charge [133, 156]. Charge interaction between such groups can modify the membrane pore size to some extent [133]. However, in general, for Donnan exclusion membranes, salt retention is lowest when pH is in the vicinity of the membrane isoelectrical point [133]. In other words, the membrane surface charge is a significant factor in the retention mechanism by charge repulsion.

2.5 Membrane hydrophobicity

The membrane contact angle is a parameter directly related to the hydrophobicity of a membrane. As can be seen in Figure 3.11, more hydrophobic membranes are less wettable by a drop of water. Consequently, hydrophobic membranes often exhibit lower water flux. In addition, hydrophobic membranes usually have greater binding potential toward hydrophobic solutes such as protein and a number of trace organics. However, hydrophobicity is essential for maintaining the membrane's mechanical and chemical stability as well as a high salt retention [157]. Membrane grafting or chemical surface modification can be used to increase the hydrophilicity of the membrane surface while preserving other essential properties within the sub-layer [144, 158].

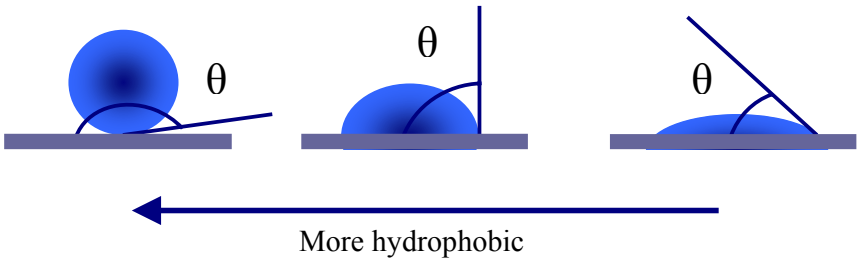


Figure 3.11: Water drop contact angle as a function of membrane surface hydrophobicity.

While contact angle is commonly used to measure the hydrophobicity of the membrane surface, the data should be used with some caution. Membrane surface roughness can influence contact angle measurements due to capillary effects and results from different measurement methods can vary considerably [16]. Several measurement methods have been reviewed elsewhere [16].

Contact angles of clean membranes selected for this study were measured using a standard technique as described by Schäfer [16]. The results are tabulated in Table 3.2. Koch membranes appear to be more hydrophilic than Trisep and Filmtec membranes. Amongst 4 Koch membranes under study, the TFC-SR2 membrane is the most hydrophobic even though it has the most permeable membrane. This is because the membrane permeability also depends on the membrane pore size and skin layer thickness. Indeed, salt retention measurements indicate that the TFC-SR2 has the lowest Ca^{2+} and Na^{+} retention amongst the 4 Koch membranes (see section 2.6). Latter membrane pore size characterisation also reveals that the TFC-SR2 is a very loose NF membrane.

Table 3.2: Contact angle of clean membranes.

Membrane	Contact angle of clean membrane (^{o})
TFC-ULP	31
TFC-S	30
TFC-SR1	19
TFC-SR2	11
X20	33
ACM4	35
XN40	39
TS80	43
NF 90	42
NF 270	55

2.6 Permeability & salt retention

Average permeability, membrane intrinsic resistance, Ca^{2+} and Na^{+} retention of the 10 membranes selected for this study are shown in Table 3.3. Both average permeability and salt retention of the selected membranes are distributed across a wide range. Sodium retention ranges from 9.8 % for the TFC-SR2 membrane to 95.7 for the X-20 membrane. The XN-40 membrane has the highest permeability amongst Trisep membranes, while the TFC-SR2 has the highest permeability amongst Koch membranes. Concomitantly the TFC-SR2 has the lowest Na^{+} retention. In fact given its very low salt retention (and large pore size as can be seen later), the TFC-SR2 is at the boundary of UF membranes in the classification chart.

Interestingly ACM-4, TS-80, and TFC-SR1 have comparable or slightly lower calcium retention (see Table 3.3) than sodium retention despite the fact that hydrated size of calcium is larger and so is its diffusion coefficient. According to Peeters *et al.* [153] these membranes can be classified as Donnan exclusion membranes. In other words, their separation process is mainly governed by Donnan interaction rather than selective diffusion between different salts [133, 153].

Table 3.3: Characteristics (pure water flux, permeability, membrane resistance, calcium and sodium retention) of the membranes used. Salt retention was obtained from stirred cell experiments except for NF-90 and NF-270 membranes.

Membrane	Average Permeability [$Lm^{-2}h^{-1}bar^{-1}$]	R_M [m^{-1}]	Calcium Retention [a] [%]	Sodium Retention [b] [%]
X20	3.8	$9.4 \cdot 10^{13}$	95.0	95.7
ACM4	5.2	$7.0 \cdot 10^{13}$	39.3	53.5
XN40	8.5	$4.2 \cdot 10^{13}$	50.3	28.0
TS80	5.2	$6.9 \cdot 10^{13}$	46.15	53.1
TFC-ULP	6.7	$5.4 \cdot 10^{13}$	77.4	74.1
TFC-S	11.0	$3.3 \cdot 10^{13}$	78.0	76.5
TFC-SR1	10.5	$3.4 \cdot 10^{13}$	20.1	28.4
TFC-SR2	15.4	$2.3 \cdot 10^{13}$	21.2	9.80
NF 90	6.4	$5.5 \cdot 10^{13}$	95.0	85.0
NF 270	13.5	$6.3 \cdot 10^{13}$	43.0	40.0

[a] Experimental condition: 1 mM of $CaCl_2$ at 5 bar, pH ~ 6.0

[b] Experimental condition: 10 mM of NaCl at 5 bar, pH ~ 6.0

3. *Selected trace contaminants& their physicochemical properties*

3.1 Representative PhACs

Given our highly developed health care system, a large number of pharmaceuticals are being used at considerable quantities for various medical reasons and health benefits. Pharmaceuticals are also applied to live stock and other animals, mostly antibiotics-sometimes to a substantial amount, in our modern day husbandry practices. A large proportion of such pharmaceuticals are unmetabolised or only partly metabolised. These are excreted via faeces and urine, in unchanged or modified forms, and are known as pharmaceutically active compounds (PhACs).

Three pharmaceuticals (or pharmaceutically active compounds) selected in this study represent three different classes of drugs. They are also amongst the most frequently detected and reported pharmaceuticals in the aquatic environment in the open literature. Sulfamethoxazole is probably the most frequently used antibacterial within the synthetic sulphonamide antibacterial drug class. It has been extensively applied for many years in human and veterinary medicines for infectious diseases and in animal feed additives to promote growth and weight gain in husbandry practice [159]. Carbamazepine is one of the most widely used antiepileptic drugs. The bulk of the administrated

prescription is metabolised in the human body and only 2-3 % of the given dose is excreted in an unchanged form. However, due to the large quantity prescribed each year and almost zero removal efficiency by conventional wastewater treatment processes, carbamazepine is quite abundant in the aquatic environment at low concentration [102, 160]. Ibuprofen is used primarily as an anti-inflammatory or analgetic agent. Its occurrence in the aquatic environment is also very widespread [102, 160, 161].

3.2 Representative steroid hormones

All vertebrates (animals with backbone) have a highly complex and delicate endocrine system, which plays an important role in growth and development. The endocrine system releases extremely small amounts of hormones that act as chemical messengers. These hormones interact with specific receptors in cells at a specific time to trigger responses and prompt normal biological functions such as growth, reproduction and development. Scientific studies have shown that some chemicals can interfere with these processes by mimicking the hormone's behaviour, interfering with hormone receptors or interfering with the production and removal of hormones [162]. These endocrine disrupting chemicals (EDCs) include hormones, synthetic industrial compounds and their metabolized products. The four natural steroid hormones selected in this study are ubiquitous in the aquatic environment, particularly in secondary treated effluent. They also possess the highest endocrine disrupting potency. Further discussion on their endocrine disrupting potency and occurrence in the environment can be found in Chapter 2.

3.3 Representative hormone mimicking compounds

Prominent amongst hormone mimicking compounds are alkyl phenols (by products of the degradation process of alkylphenol ethozylates) and bis-phenol A. Alkylphenol ethoxylates (APEs) with a current annual production rate of 360,000 tones world wide [163], are widely used in domestic detergents, pesticide formulation and many other industrial products. In wastewater treatment plants or in the environment, they degrade into more persistent alkylphenols (APs) such as nonylphenol (NP), octylphenol (OP) and other compounds with a shorter chain. 2,2-Bis-(4-hydroxyphenyl)propane (Bis-phenol A or BPA) is one of the most important and most extensively produced organic chemicals. In 1993, the world annual production of BPA amounted to 1.1×10^6 tones [164]. BPA production is a fast growing market with an annual increase rate of approximately 5%. Although BPA is mainly used to produce polycarbonates (PC), epoxy resins (ER), flame retardants, and other products in the plastic industry, it is one of the most frequently occurring EDCs in wastewater, surface waters, sewage sludge, and waste disposal leachates.

3.4 Trace contaminants

The focal point of this study is the emergence of trace organic contaminants of high concern in the aquatic environment, particularly in the water recycling practice. Therefore, ten notable trace organics representing three different contaminant classes were selected for this study. They are sulfamethoxazole, carbamazepine, and ibuprofen - representing pharmaceuticals and pharmaceutically active compounds; nonyl phenol, tert-butyl phenol, and bis-phenol A - representing hormone mimicking compounds; and estradiol, estrone, progesterone, and testosterone - representing natural steroid hormones. Their molecular structures are presented in Figure 3.12.

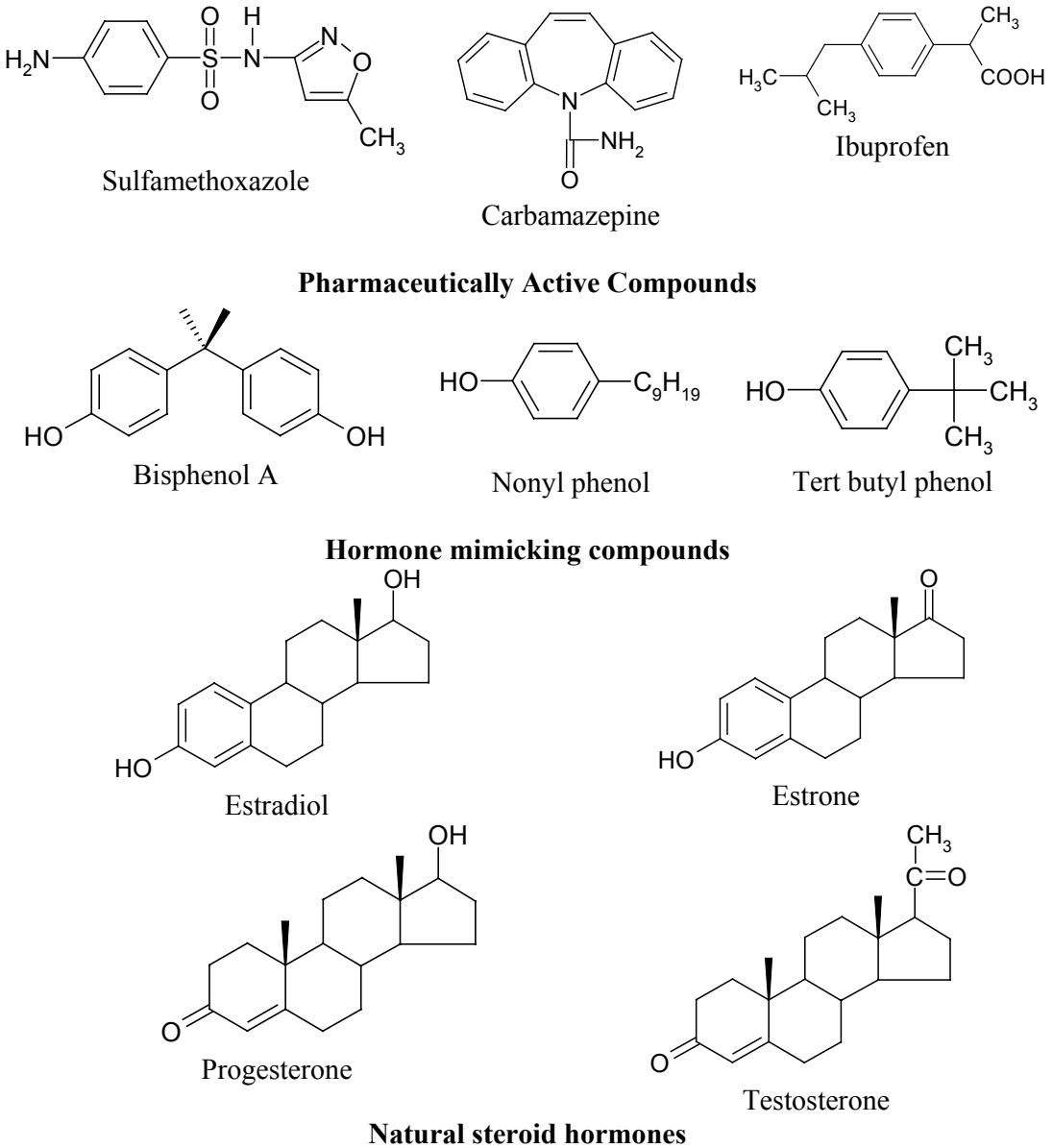


Figure 3.12: Molecular structure of trace organic contaminants selected in this study.

3.5 Physicochemical properties

Molecular weight and several other physicochemical properties including solubility in water, pK_a, log K_{ow}, and dipole moment of the 10 selected trace organics are presented in Table 3.4. These selected compounds are low molecular weight organics within the range from 150 g/mol to 315 g/mol. As data on small molecular weight trace organics retention by NF/RO membrane filtration processes are still very rare, data presented in this study would be significant in predicting membrane performance.

Table 3.4: Physicochemical properties of trace contaminants used in this study

Compound	Molecular weight (g/mol)	Solubility in water (mg/L)	pK_a	Log K_{ow} [h]	Dipole moment [i] (debye)
Sulfamethoxazole	253	610 [a]	5.7	0.89	5.356
Carbamazepine	236	17.7 [b]	2.3	2.45	3.588
Ibuprofen	206	49 [c]	4.9	4.13	1.800
Tert butyl phenol	150	700 [d]	10.2	3.31	1.010
4-Nonyl phenol	220	5 [e]	10.3	5.77	1.005
Bis-phenol A	228	120 [f]	10.1	3.32	1.411
Estradiol	272	13 [g]	10.4	4.01	1.409
Estrone	270	13 [g]	10.4	4.54	3.695
Testosterone	288	na	na	3.84	3.530
Progesterone	315	na	na	4.63	3.501

[a] Ref: [165]
[b] Ref: [166]
[c] Ref: [167]
[d] Ref: [168]
[e] Ref: [169]
[f] Ref: [170]
[g] Ref: [171]
[h] Ref: determined using a commercial software (Pallas 3.0 [172]). Note: It is assumed that the calculated values are corresponding to neutral species of the compounds.
[i] Ref: determined using a commercial software (Hyperchem [173])
na: Not applicable or data not available

Log K_{ow} shows the hydrophobicity of the compound, with zero being the most hydrophilic and larger log K_{ow} indicates greater hydrophobicity. Most of the selected trace organics, except sulfamethoxazole and carbamazepine, have relatively high log K_{ow}. This indicates that they would readily adsorb to hydrophobic materials. Dipole moment is directly related to the polarity of the compound. Given that the membrane surface carries fixed charged groups, it has been hypothesized that highly polarised compounds (dipole moment of greater than 3) can approach the membrane pore in an orientated way, hence, their retention can be lower compared to other compounds with similar molecular weight [126]. Clearly, one would expect this dipole effect to take place when the compound is cylindrical in shape rather than spherical.

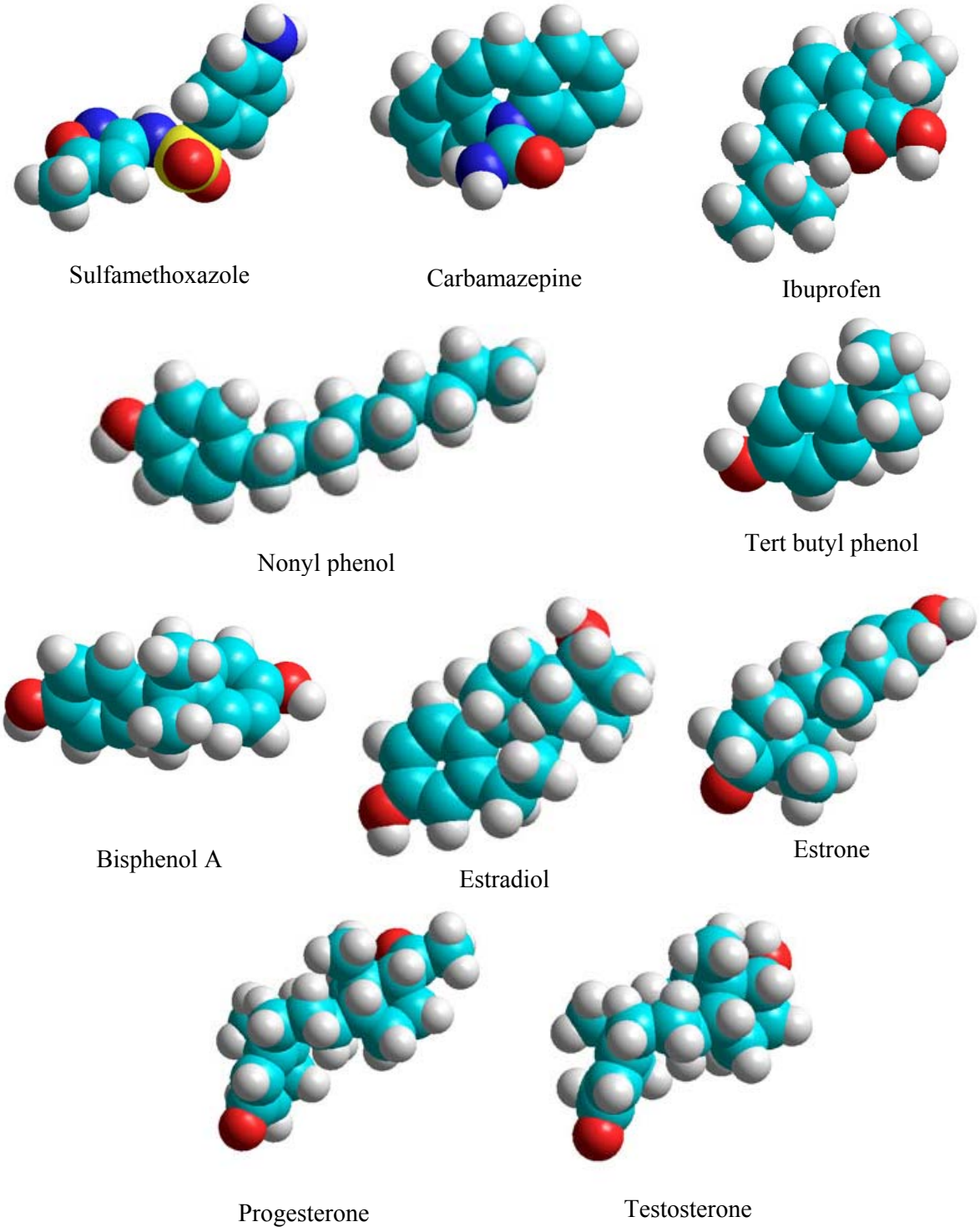


Figure 3.13: 3-dimenstional shapes of trace organics selected in this study. (Optimisation process was carried out using a commercial software (Hyperchem [173]). Ibuprofen geometrical shape was not optimised due to software limitation.)

Molecular structures of selected compounds were planarity plotted. The molecular 3-D shape was then obtained by optimising the compound free energy using commercial software Hyperchem [173]. 3-D computer constructed images of the 10 selected trace organics are shown in Figure 3.13.

4. *Chemicals & background solution*

4.1 Background solution

Experiments were conducted in deionised water or in a background buffer solution. The background solution was selected to represent a simple model of background electrolyte of environmental water. The composition of the model system is summarised in Table 3.5. Unless otherwise stated, this solution was used for all experiments where background electrolytes were utilised. For some experiments, 1 M NaOH or HCl were used to adjust the solution pH. These chemicals and those listed in Table 3.5 were of analytical grade from Sigma-Aldrich (Saint Louis, MO) or Fisher Scientific (Pittsburgh, PA).

Table 3.5: Background buffer solution composition.

Chemical	Molecular Weight (g/mol)	Concentration (mM)	Concentration (mg/L)	Purpose
$NaHCO_3$	84	1	84	Buffer capacity
NaCl	58.5	20	1170	Background electrolyte

4.2 Natural organic matter

Several types of organic matter were selected in this study. Suwannee River natural organic matter (SRNOM) and reference fulvic acid (FA) were purchased from the International Humic Substances Society (St. Paul, MN) and used to represent natural organic matter (NOM) in some experiments. SRNOM and reference FA were selected because of their high concentration of dissolved organic carbon and low concentration of inorganic salt (ash content of 7% and 0.4% for SRNOM and FA, respectively). Contribution of this ash to the solution ionic strength is expected to be negligible.

Several experiments in this study used organic matter, which was concentrated from Mooney Mooney Dam (Brisbane National Park, NSW, Australia) in a previous project [16]. This NOM was obtained by concentrating the wed using microfiltration (MF) and reverse osmosis (RO) membranes followed by freeze drying. The concentrating procedure and characterisation of this NOM have been described in detail elsewhere [16]. Aldrich humic acid (HA) (from Sigma-Aldrich, Saint Louis, MO) was used for comparison in some experiments. This HA is in fact from soil humid and

not from an aqueous source, but nevertheless frequently used in the literature. Unless otherwise stated, in all experiments where organic matter was used, the concentration in the feed solution was 10 mg/L. The concentration was confirmed by measuring total organic carbon (TOC) of the feed solution.

Secondary treated effluent was obtained from Brendale wastewater treatment plant in Queensland, Australia. Analysis of the water shows that it contains approximately 10 mg/L of TOC, 50 mg/L of sodium, and 10 mg/L of calcium. Detailed composition of this secondary effluent is available elsewhere [174].

4.3 Natural steroid hormones

Four radiolabeled steroid hormones, estradiol, estrone, progesterone, and testosterone were selected for this study. Estradiol-2,4-^{3}H-(N) and progesterone-2,4,6,7-^{3}H-(N) were purchased from Sigma-Aldrich (Saint Louis, MO), while estrone-2,4,6,7-^{3}H-(N) and testosterone-1,2-^{3}H-(N) were purchased from Perkin Elmer (Boston, MA).

The radiolabeled hormones were supplied in ethanol solution and were diluted with DI water prior to use. Specific radioactivity of estradiol, estrone, progesterone, and testosterone were 17, 65, 88, and 55 Ci/mmol, respectively. The stock solutions were stored in the dark at < 4°C. All hormones had radiochemical purity higher than 97% at the time of purchase. Experiments were completed within 5 months from the time of purchase. According to the manufacturers, it is estimated that the purity decreases approximately 2-5% each year, as these are unstable products [175, 176].

4.4 Hormone mimicking compounds & pharmaceuticals

The hormone mimicking compounds (nonyl phenol, bisphenol A, and tert-butyl phenol) and pharmaceuticals (sulfamethoxazole, carbamazepine, and ibuprofen) were purchased from Sigma-Aldrich (Saint Louis, MO). These chemicals are of analytical grade and are reported to be of 99 % purity or higher. Stock solutions (1 g/L) were prepared in pure methanol for all three pharmaceuticals. The stock solutions were stored at < 4 ^{o}C and were used within 1 month.

5. *Analytical techniques*

5.1 General analytical methods

Standard laboratory instruments were used for the measurement of pH and conductivity. A Perkin-Elmer Optima 3000 ICP-AES instrument was used to determine the cation content of solutions.

Samples were diluted with 5% nitric acid. All vials used were cleaned with 1 M nitric acid. ICP-AES multielement standard (Merch, Germany) was used to prepare the calibration curve for each analysis. Total organic carbon (TOC) of the solution was analysed using a Shimadzu TOC-V CSH analyser. Analysis was conducted in a non-purgeable organic carbon mode (NPOC) and the samples were acidified using HCl acid and purged for 1.5 minutes prior to injection.

5.2 Natural steroid hormone analysis

Radiolabeled hormones were analyzed using a Perkin Elmer scintillation counter (Tri-Carb 2900 TR). Scintillation vials (20 mL) were filled with 1 mL of sample and 9 mL of Ultima Gold® scintillation cocktail (Perkin Elmer, Boston, MA). Prior to analysis, the vials were shaken vigorously and the samples were counted for 5 minutes. A set of calibration standards at concentrations of 0, 0.01, 0.1, 1, 10, 100, and 1000 ng/L of each hormone were prepared from fresh compounds. Hormone concentration was determined based on a linear regression of the calibration standards. With this method, the detection limit was approximately 0.5 ng/L for estradiol, and 0.1-0.2 ng/L for the remainder of the hormones.

5.3 Hormone mimicking compounds & pharmaceuticals

A Shimadzu HPLC system equipped with a Supelco Drug Discovery C-18 column (4.6 mm - 150 mm, 5 μm), and UV-V detector was used to analyze concentration of hormone mimicking compounds and pharmaceuticals in the feed and permeate samples. A detection wavelength for carbamazepine was 225 nm and for all other compounds was 280 nm. The mobile phase for gradient elution was deionized water (buffered with 0.025 M KH_2PO_4) and acetonitrile (ACN) – delivered at a constant flow rate of 1 ml/min. A gradient program of the mobile phase was set in accordance with the chromatographic behaviour of respective analytes. A sample injection volume of 50 μL was used, and a typical quantification limit for all analytes under these conditions was approximately 20 μg/L. Standard curves yielded coefficients of determination (R^2) greater than 0.98 within the range of experimental concentrations in all cases. Analysis was carried out immediately following filtration experiments.

6. *Filtration equipment & experimental protocols*

In this study, all filtration experiments were carried out using lab-scale filtration equipment with a flat sheet membrane cell holder. Dead end stirred cell was used primarily for screening purposes and for adsorption studies. Three cross flow NF/RO membrane test units namely ANSTO, Yale, and Wollongong systems, were used in this project. This is because of the relocation of the

candidate. However, extra caution has been made when interpreting the data to minimise any inconsistency in cross flow cell geometry and system arrangement. Details of the filtration equipment and experimental protocols are presented below. Further information to clarify the experimental procedures in each of the subsequent chapters will also be included.

6.1 Stirred cell

A picture of the stirred cell system used in this study is shown in Figure 3.14. The inner diameter is 56.6 mm resulting in a membrane surface area of 21.2×10^{-4} m^2. A magnetic stirrer (Amicon) was used with the stirrer speed calibrated using a stroboscope. Stirrer speed was fixed at 400 rpm to minimise polarisation concentration effect. The pressure was set and maintained using an instrument-grade air cylinder. Permeate was collected on a PC-controlled electronic balance.

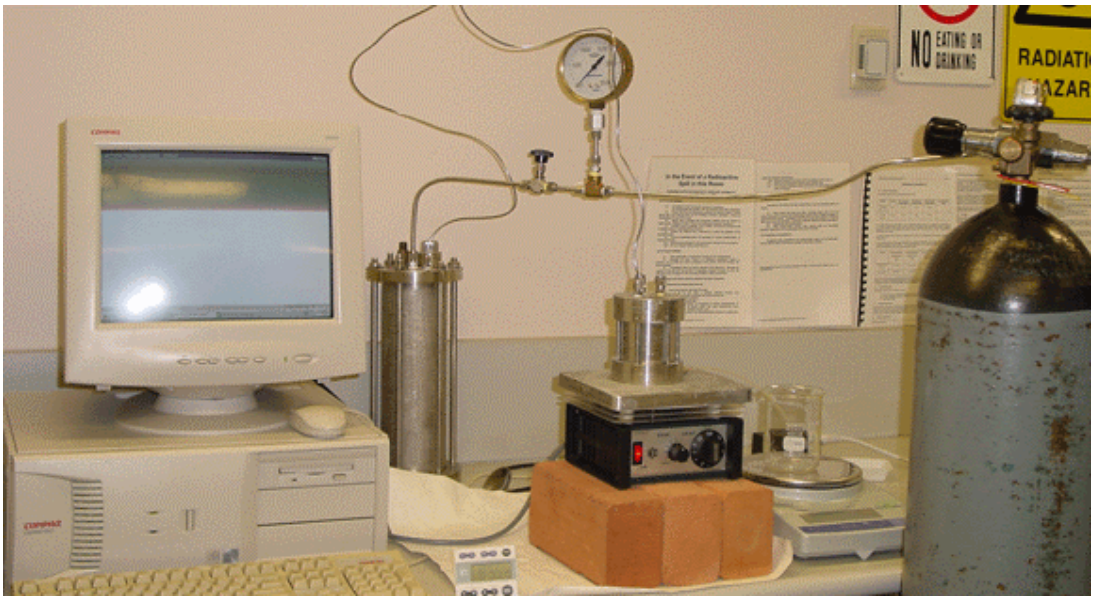


Figure 3.14: Stainless steel stirred cell set up.

Prior to any experiments, the membrane was compacted for at least 1 hour at 10 bar and the pure water flux was measured at 5 bar for 30 mins. A feed solution of 185 mL in volume was then placed in the stirred cell. In total, 120 mL of the feed was filtered which gives a threefold concentration in the cell for fully retained species. Six permeate samples of 20 mL each were taken.

6.2 ANSTO cross flow NF/RO test unit

The ANSTO cross flow NF/RO filtration test unit includes a SEPA® cross-flow cell (Osmonics), a feed pump, a recirculation pump (Micropump), and a digital flowmeter. A pressure dampener is used to avoid pulsation. A schematic diagram and a picture of the unit are shown in Figure 3.15 and

Figure 3.16, respectively. The effective membrane surface area is 138.7 cm^2 (146 mm x 95 mm) and the channel height is 0.86 mm. Prior to the experiment with the cross flow system, the membranes were gently washed with DI water to remove the protective coating and a new membrane was used for each experiment.

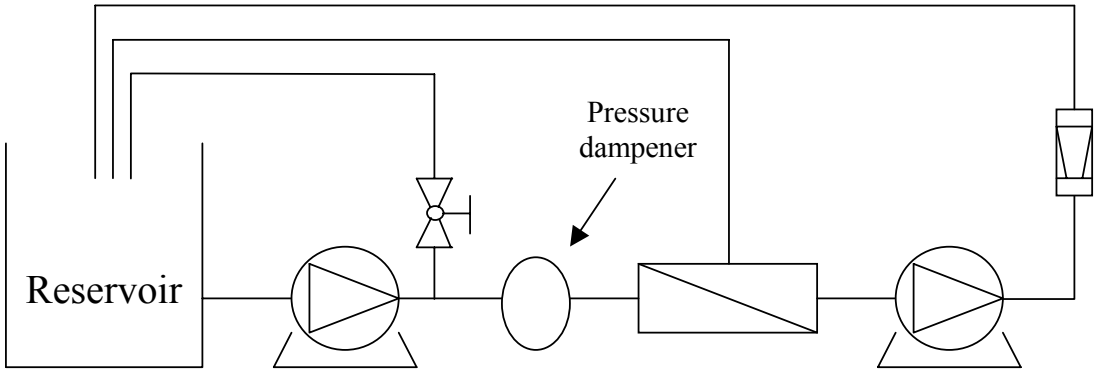


Figure 3.15: Schematic diagram of the ANSTO cross flow NF/RO filtration test unit.

Prior to any experiments with this filtration system, the membranes were compacted for at least 1 hour using DI water at 10 bar. Pure water flux was then determined at the end of the compaction process. The feed reservoir was then emptied and the system was drained out to avoid dilution. The feed reservoir was then refilled with the test solution. The applied pressure was 10 bar and both permeate and retentate were recycled to the feed reservoir, unless otherwise stated. Permeate and feed samples were collected for analysis at specified intervals.

Figure 3.16: ANSTO cross flow NF/RO filtration equipment.

6.3 Yale cross flow NF/RO test unit

The Yale cross flow NF/RO test unit includes a Dayton capacitor start motor (Dayton Electronic Manufacturing Co., Chicago, IL) coupled with a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN) capable of providing pressures up to 69 bar and at a flow rate of 4.2 L/min. Temperature of the feed reservoir was controlled using a chiller/heater (Neslab RTE 111). Duplicate plate-and-frame membrane cells were used, each housed a membrane coupon with an identical effective surface area of 23.1 cm^2 (77 mm × 30 mm). The membrane channel height is 2 mm. Permeate flow rate was monitored by a digital flow meter connected to a PC and crossflow rate was monitored by a rotameter. A schematic diagram of the system is shown in Figure 3.17. All test unit parts in contact with the solution are made of stainless steel or Teflon to minimize adsorption of the organic compounds used.

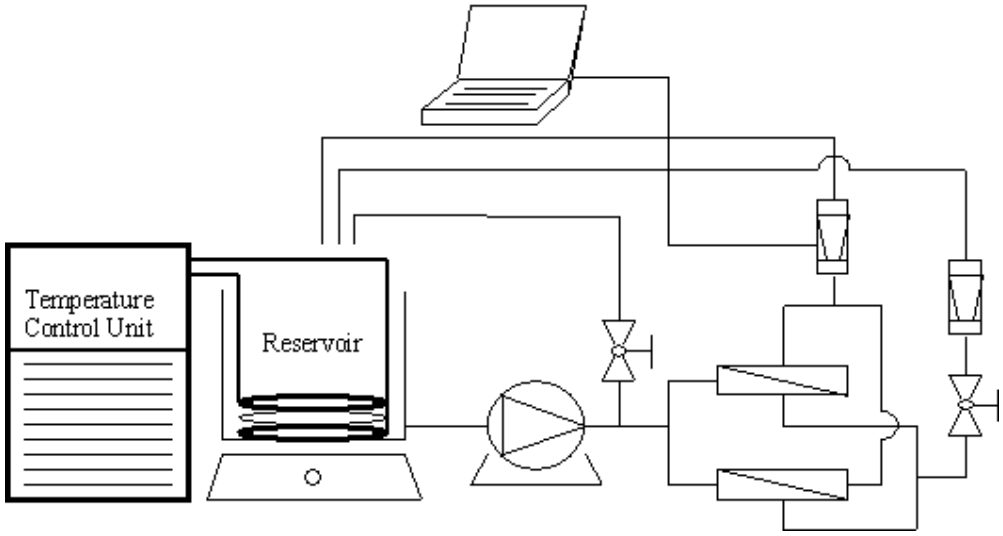


Figure 3.17: Schematic diagram of the Yale cross flow NF/RO filtration test unit.

Prior to any experiments with this system, the membrane was stabilized at 12 bar (176.4 psi) using DI water for at least 16 hours until the permeate flux attained a constant value. Tested solution was then introduced to the feed reservoir. The feed reservoir temperature was kept at 20±0.1^{o}C throughout the experiment. Unless otherwise stated, permeate was recycled back to the feed reservoir.

6.4 Wollongong cross flow NF/RO test unit

The Wollongong cross flow NF/RO filtration test unit was designed and built to achieve a similar geometry and hydrodynamic condition as the Yale system. Seawater grade stainless steel was used

for the fabrication of the cross flow cell. A picture of the cross flow cell and the system schematic diagram are shown in Figure 3.18 and Figure 3.19, respectively.

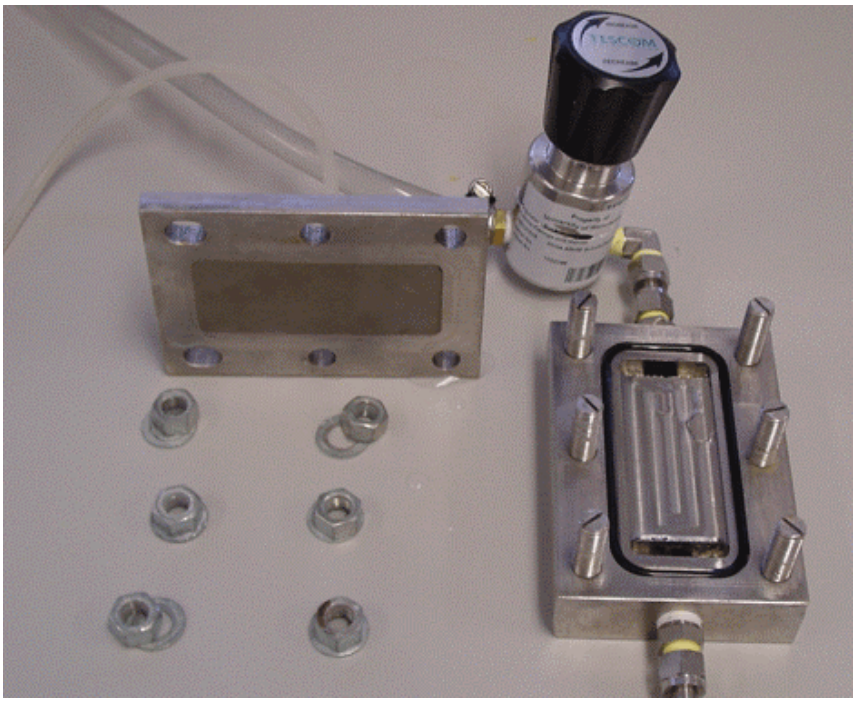


Figure 3.18: Stainless steel cross flow cell of the Wollongong NF/RO filtration test unit.

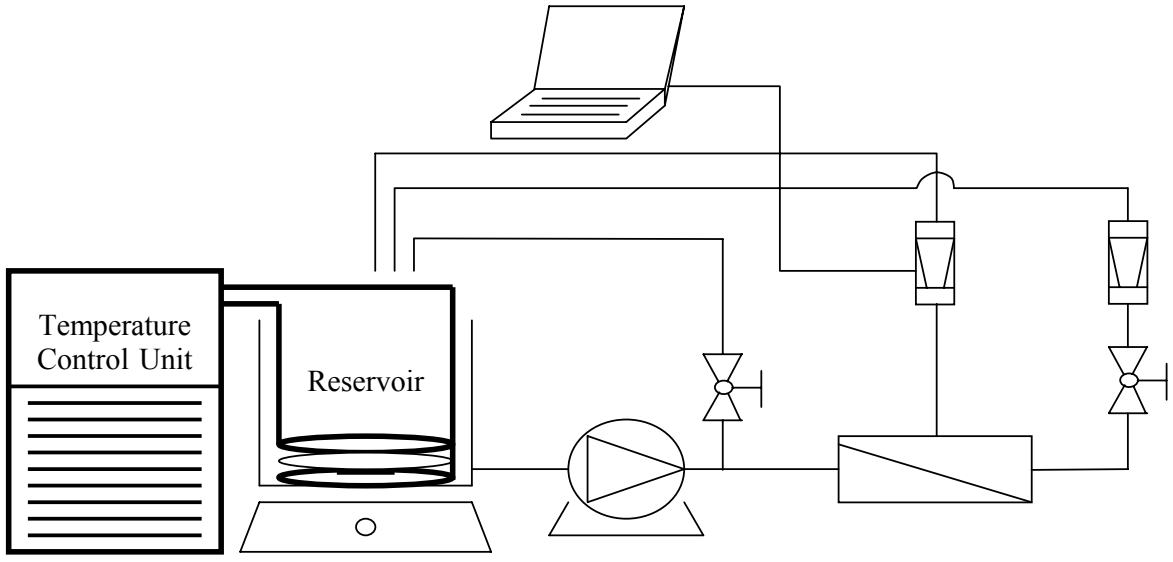


Figure 3.19: Schematic diagram of the Yale cross flow NF/RO filtration test unit.

Effective membrane area of this cell is 40 cm^2 (40 mm x 100 mm). The membrane channel height is 2 mm. Similar to the Yale cross flow test unit, this unit is also equipped with a Hydra-Cell pump

(Wanner Engineering Inc., Minneapolis, MN) capable of providing pressures up to 69 bar and at a flow rate of 4.2 L/min. A Neslab RTE7 is used to control the filtration solution temperature. Other components of the filtration system are the same as that of the Yale system. A filtration protocol similar to that of the Yale system is adapted for this test unit. Unless otherwise stated, permeate was also recycled back to the feed reservoir.

7. *Conclusions*

In this chapter, physicochemical properties of the selected membranes and trace organic contaminants were described in detail. The ten selected membranes were good representatives of the wide spectrum of the NF and RO membranes with their salt retention spanning from almost negligible (very loose NF membrane) to very high (high salt retention RO membrane). The nine selected organics represented three of the most prominent classes of emerging water and wastewater trace contaminants. As discussed above, their physicochemical properties are quite distinct from one another. The chapter also included details of the filtration systems, associated experimental protocols, and analytical techniques.

Chapter 4

Steric interaction

1. *Introduction*

For porous membranes, the membrane pore size and pore size distribution relates directly to both water flux and separation characteristic. Consequently, it becomes one of the most important performance parameters. In parallel with the history of membrane filtration development, there have been many of scientific studies devoted to the understanding and characterisation of membrane morphology such as pore shape and size, pore size distributions, pore density, pore length, cross-sectional structure of the pores, etc. Several comprehensive review articles on this topic have also been written [177-180]. However, the membrane morphology is truly a complex matter, one that still requires many more dedicated research works. Despite its great importance, the membrane pore size is not usually available from the membrane manufacturers. This is particularly true for nanofiltration and to a lesser extent ultrafiltration membranes. Instead, membrane users have to rely on the molecular weight cut-off (MWCO) value as a rough indicator to predict membrane retention. MWCO is defined as the molecular weight of a neutral organic solute that corresponds to membrane retention of 90 % [125]. It is noteworthy that MWCO values of most NF membranes are in the range between 200 to 300 Da, which coincides with the molecular weight of many trace organics of concern. The sieving (or size exclusion) mechanism is expected to play a primary role in the removal mechanisms during nanofiltration of such contaminants. Consequently, it is essential to first characterise the membrane pore size and use it as a benchmark to elucidate other removal mechanisms.

This chapter aims at examining the role of steric hindrance transport in removing trace organics in nanofiltration processes. Although various membrane pore size (and pore size distribution) characterisation methods are currently available, most of them were developed prior to the introduction of nanofiltration membranes and are therefore more suitable for large pore size membranes where diffusive transport within the membrane pore is negligible for small molecules. Nonetheless, this chapter will provide a brief overview of most membrane pore size characterisation

techniques. A steric hindrance model has been developed based on the hydrodynamic approach for the characterisation of the membrane pore size. Trace organic retention was then related to the membrane morphology and the mechanisms of trace organic retention and transport through the NF membrane were delineated and discussed in detail.

2. *Pore size & pore size distribution*

2.1 Characterisation techniques

Comparing products provided by different manufacturers is an enormous challenge for most membrane end-users. Although MWCOs are available for some membranes, the measuring processes for these MWCOs do not follow any standard procedures. Consequently, two membranes with the same MWCO value may have quite different pore size and performance characteristics. Driven by the need to better understand the membrane performance, various methods to characterise the pore structure of porous membranes have been developed. They can be grouped into two categories: i) physical methods and ii) methods based on reference organic solute transport through the membrane pores.

2.2 Physical methods

Physical methods do not directly relate to the solute permeation through the membrane pores, which is the most important characteristic of separation membranes. Well-known physical methods for pore size characterisation are [178]:

- Microscopic method,
- Bubble pressure and gas transport method,
- Permporometry (or gas-liquid method), and
- Thermoporometry (or liquid-solid method)

The microscopic method was developed with the introduction of electron microscope techniques. Visual information of the membrane surface and cross-sectional structure can be obtained at a very high resolution. Theoretically, such resolution can be sufficient to examine NF membranes with relatively small pore size. However, difficulties associated with sample preparation and fine tune of the instrument have largely hindered the usefulness of this method for NF membranes. It is noteworthy that membrane samples must be coated with conductive material such as gold, chromium, or carbon prior to microscopic analysis, either with a scanning electron microscope (SEM) or transmission electron microscope (TEM). The membrane samples are therefore dry and shrinkage may occur [181, 182]. Furthermore, membrane swelling in an aqueous environment cannot be accounted for. This limitation can be overcome with an atomic force microscope, a

useful instrument that allows imaging of non-conductive surface with nm-scale resolution in both air and liquid environments. AFM has been used quite extensively to characterise the pore size and pore size distribution of porous membranes. Although AFM application can be extended to NF membranes [148, 183], caution should be taken when interpreting the results [152]. The smallest available AFM tip has a diameter in the range of tens of nm. This is comparable or larger than the membrane surface roughness and significantly larger than the membrane pore. Therefore, this technique can be prone to imaging artefacts when probing small pore size membranes.

The last three physical methods for pore size characterisation mentioned above were developed prior to the introduction of NF membranes. Although they are frequently used techniques for more open pore membranes such as MF and UF, they are generally unsuitable for NF membranes. However, as the boundary between UF and NF membranes is rather blurred (indeed, many membrane texts still treat NF as a subset of UF membranes), it is still worth reviewing such techniques briefly here. The bubble pressure and gas transport method evaluates the membrane pore size by measuring the pressure necessary to force a liquid through a water-swollen membrane or the gas flow rate through the membrane, respectively. The permporometry (or gas-liquid method) is based on a well-known phenomenon of capillary condensation of liquid in micropores. At a particular pressure, capillary condensation block prevents unhindered gas transport through the membrane pores. When the pressure is reduced, pores having a size corresponding to the applied pressure are empty and become available for gas transport. By measuring the gas flow rate against the applied vapour pressure, the membrane pore size and pore size distribution can be determined. Based on a phenomenon that freezing and melting point of a liquid is lower in smaller pores, the thermoporometry method determines the pore size and its distribution by measuring the phase change thermodiagram of that liquid in the membrane pores. Further detail about these pore size characterisation methods can be found in a review article by Nakao [178].

With the exception of the microscopic method, other physical methods tend to overestimate the membrane pore sizes. Zeman et al., [184, 185] evaluated the pore size of three polysulphone UF membranes. They found that the pore radii were 20–30 nm when using the thermoporometry technique, while they were approximately 2–3 nm based on an SEM examination. Dextran retention of these membranes appears to be in good agreement with SEM results.

2.3 Reference solute transport

Pore size characterisation based on reference solute transport through the membrane is probably the most popular method for NF and UF membranes. In this method, the transport phenomenon of a reference solute through the membrane pore is mathematically described. It is then possible to obtain information about the membrane pore and its distribution based on volumetric permeate flux and solute retention from a set of filtration experiments. Three notable approaches have been used to develop such mathematically descriptive models. The first approach is based on the well-known irreversible thermodynamic principle derived by Kedem and Katchalsky [186] and Spiegler and Kedem [187] in the early 60s. The second approach is based on the generalised Fickian diffusion equations and is often referred to as the Stefan-Maxwell multicomponent diffusion equations [188]. Although represented by different set of equations, these two approaches are in fact equivalent [180, 188]. The last approach is called the hydrodynamic model or pore model, which is essentially based on the pioneering work of Ferry in 1936 [189]. This approach differs fundamentally from the classical thermodynamic and Stefan-Maxwell approaches commonly used in reverse osmosis. While the thermodynamic and Stefan-Maxwell approaches consider the membrane to be a "black box" when deriving the phenomenological equations [178, 186, 188], the hydrodynamic approach assumes a geometrical model of a membrane, and derives all the transport equations and properties based on this geometry [177]. The mathematical description of these three approaches is examined in the next section.

3. *Theory of the transport phenomena*

3.1 Irreversible thermodynamic model

The irreversible thermodynamic approach treats the membrane as a black box, which relates driving forces to permeate and solute fluxes. It is probably the most well documented theory used to examine transport phenomena in reverse osmosis and to a lesser extent in NF and UF membrane filtration processes. The final form of volume and solute fluxes, J_v and J_s, respectively can be expressed as:

$$J_v = P_h(\Delta P - \sigma\Delta\Pi) \tag{4.1}$$

and

$$J_s = -PL\frac{dC_s}{dz} + (1-\sigma)J_v C_s \tag{4.2}$$

where P_h and P are hydraulic permeability and solute permeability, respectively. ΔP, $\Delta\Pi$, L,C_s, z are transmembrane pressure, osmotic pressure, membrane active layer thickness, solute concentration, and the axial position of the solute perpendicular to the membrane layer, respectively. Sigma (σ) is

called the reflection coefficient, an important parameter when examining solute transport phenomena using irreversible thermodynamic or Stefan-Maxwell approaches. It represents the maximum real retention of a particular solute by the membrane. The definition of real retention is described in section 4.2 (page 71).

3.2 Stefan-Maxwell model

Stefan-Maxwell approach is most popular for the study of multicomponent gaseous diffusion processes. It relies on a simple principle that the sum of the forces exerted upon molecules is balanced by the friction the molecule experiences from others [180]. This approach has also been applied to liquid filtration processes, although its popularity is low due partly to its mathematical complexity. Peppas and Meadows provide a complete derivation of the Stefan-Maxwell equations [188]. The final form of the solute flux is expressed in the model as follows:

$$J_s = -D_2 C x_s \frac{d\ln(x_s \gamma_s)}{dz} + \frac{D_2}{D_1} J_v C\ x_s \qquad (4.3)$$

where x_s is solute mole fraction, C is the total molar concentration, γ_s is the solute activity coefficient. For an ideal solution, γ_s equals to unity. D_1 and D_2 are over all transport coefficients given in term of the binary Stefan-Maxwell diffusivities as follows [180]:

$$\frac{1}{D_1} = \frac{1}{D_{sw}} + CV_s \frac{x_m}{D_{wm}} \qquad (4.4)$$

and

$$\frac{1}{D_2} = \frac{x_s}{D_{sw}} + \frac{x_m}{D_{sm}} \qquad (4.5)$$

where D_{sw} and D_{sm} are diffusion coefficient of solute in water and in membrane phase, respectively. V_s is specific volume of the solute, and x_m is solute mole fraction within the membrane polymer.

Combining Eqs. 4.3-4.5, the reflection coefficient of the membrane is given as:

$$\sigma = 1 - \frac{D_2}{D_1} \qquad (4.6)$$

3.3 Hydrodynamic model

Unlike reverse osmosis membranes, it is widely accepted that nanofiltration membranes are porous. From this point of view, one can assume that solute transports through nanofiltration membranes via capillary pores. Consequently, the hydrodynamic model (or pore model) can be applied to

explain and examine the transport phenomena. In contrast to the black box approach of the irreversible thermodynamic and Stefan-Maxwell models, the hydrodynamic model is closely supported by physical explanation, and therefore has been widely used for membrane pore size characterisation studies [122, 190-194]. However, a number of assumptions must be made in order to allow the mathematical derivation of the models.

1. The membrane is modeled as a bundle of cylindrical capillary tubes, all having the same radius r_p and length L, which is much greater than r_p.

2. Furthermore, it is assumed that solute particle has a spherical shape, as is the case with all microscopic transport models involving low molecular weight solutes [177]. Although it is possible to determine the dimensions (length and width) of a rigid organic solute [69, 195], taking into account such dimensions would result in a much more intricate model. Our spherical solute assumption also accounts for the fact that the solute enters the membrane pore in a random rather than an orientated fashion.

3. A Poiseuille flow is assumed inside the membrane pores.

4. The filtration rate is constant during the experiment and a steady-flow is assumed.

5. The solution is very dilute and there is no interaction among solute molecules inside the pores.

In general, discrepancy due to the last two assumptions can be negligible for trace contaminant removal studies provided that experiments can be run for a sufficient period of time at a stable stage. The validity of the third assumption becomes questionable for very narrow pores, which are comparable to the size of a water molecule. As a result, the hydrodynamic model should not be applied for reverse osmosis membranes. The validity of the first two assumptions, namely uniform cylindrical pores and rigid spherical solute molecules are indeed quite uncertain. Except track-etch membranes, membrane pores are usually random in shape and size. They can also be randomly connected within a porous layer of the membrane. Similarly, solute molecules are dimensional and their shape and size can even vary in accordance to the solution chemistry. Despite this shortcoming, the hydrodynamic model remains very useful as proven by numerous studies. This is because the model allows an estimation of the membrane representative average pore size, which

eventually eliminates the discrepancy of these two assumptions. Attempts to introduce molecular width and length to the model to relax the second assumption have also been made [13]. The result is promising although shape of the membrane pores has not been addressed and this underlying shortcoming of the model remains unchallenged. It is noteworthy that other than the circular cylindrical, the complete model can also be developed for split pores or pores that are made of two parallel planes [177].

According to the hydrodynamic model, the driving force for diffusion or the gradient in chemical potential can be viewed as a body force exerting upon the solute. Driving forces for a solute in a cylindrical pore can be expressed in terms of both diffusive and convective components. The physical situation within the pores can be depicted in Figure 4.1. Work done on hydrodynamic modelling has been summarised in great detail by Deen in a review article in 1987 [177]. Deen derives the initial expression of the hydrodynamic as follows:

$$J_s = -K_d D_\infty \frac{\partial c}{\partial z} + K_c V c \qquad (4.7)$$

where K_d and K_c are hindrance factors for diffusive and convective transport, respectively. Although based on the same principle and physical interpretation, different versions of the hydrodynamic models can be developed depending on how the hindrance factors within the pore is accounted for.

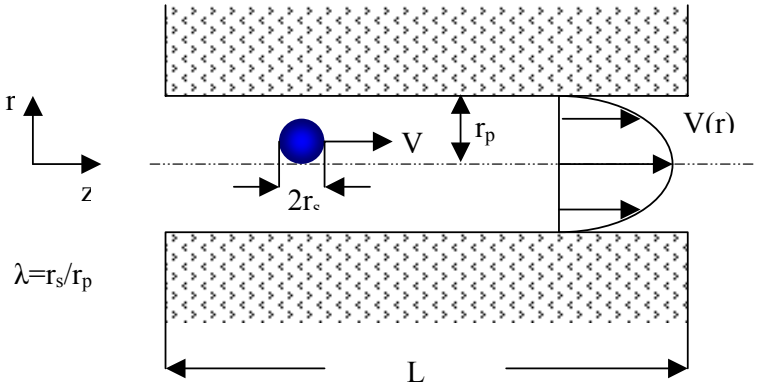


Figure 4.1: Spherical solute in a cylindrical pore (adapted from [177]).

3.4 Concentration polarisation and retention definitions

In any membrane filtration processes, the solute is rejected by the membrane and the concentration at the membrane surface is higher than the bulk solution. This phenomenon is known as concentration polarisation (CP) and depicted in Figure 4.2.

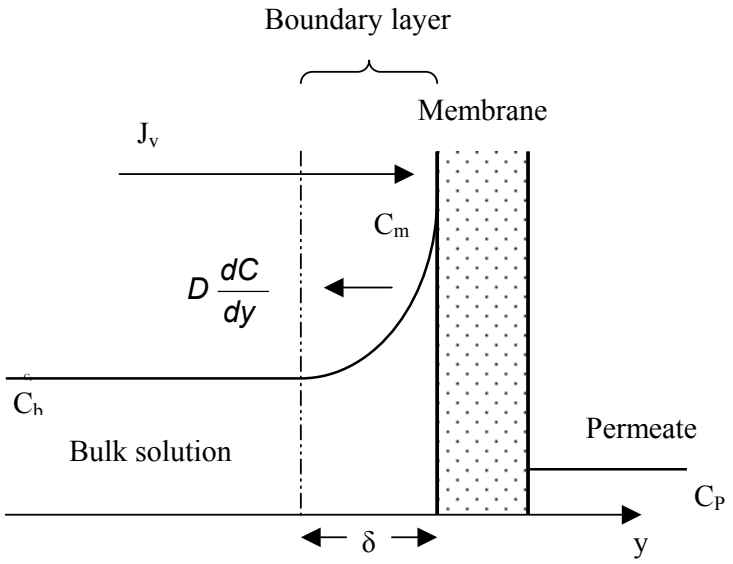


Figure 4.2: Schematic of concentration polarisation.

The separation ability of the membrane can be represented by the real retention R_r, which is defined by the relationship between solute concentration in the permeate C_p and solute concentration at the membrane surface C_m.

$$R_r = 1 - \frac{C_P}{C_m} \tag{4.8}$$

Although C_m cannot be directly measured, it can be calculated from the bulk concentration by taking a one-dimensional mass balance across the CP layer at a steady-stage.

$$J_v C - D\frac{dC}{dy} - J_v C_P = 0 \tag{4.9}$$

Integrating Eq. 4.9 over the concentration polarisation layer thickness δ, with the boundary conditions $C=C_m$ at y=0 and $C=C_b$ at y= δ, a linear relationship between C_m and C_b can be obtained:

$$\ln\frac{(C_m - C_P)}{(C_b - C_P)} = \frac{J_v \delta}{D} \tag{4.10}$$

Rearranging this, we obtain a direct expression of solute concentration at the membrane surface:

$$C_m = C_b\left\langle (1 - R_0) + R_0 \exp\left(\frac{J_v}{k_f}\right)\right\rangle \tag{4.11}$$

where R_0 is the measurable observed retention, which is defined as $R_0 = 1 - \frac{C_P}{C_b}$ and k_f is the mass transfer coefficient (k_f=D/ δ). The challenge now is to determine the mass transfer coefficient, which basically depends on the hydrodynamic condition of the experiment and diffusivity of the solute. Given the maturity of the fluid mechanic discipline, various models to evaluate mass

transfer coefficient exist. However, these models result in empirical equations that strongly depend on the system geometry, with which such equations have been derived. A total of seven of such equations can be found in a comprehensive reviewing work by Nakao [179]. Discrepancy is unavoidable when using those equations due to the difference in experimental set-up. Fortunately, the mass transfer coefficient can also be determined experimentally following a simple method as described by Sutzkover et al. [196]. Details of the mathematical derivation can be found in their publication [196] and the final form of the expression used to determine k_f is given as:

$$k_f = \frac{J_{salt}}{\ln\left[\frac{\Delta P}{\pi_b - \pi_p}\left(1 - \frac{J_{salt}}{J_w}\right)\right]} \qquad (4.12)$$

With this technique, k_f was determined first by measuring the pure water flux and the applied pressure needed to obtain the same flux for a predefined salt concentration solution. The obtained k_f value must be recorrected against the diffusivity of the actual solute under study, which may introduce additional error to the model. Nevertheless, this experimental technique appears to be superior over empirical equations.

3.5 Unifying the models

Combining the solute and solvent fluxes, one can obtain an expression for real retention for each of the models mentioned above. It has been revealed that these three models are in fact analogous to one another based on their mathematical forms as can be seen in Table 4.1 [180]. As illustrated above, real retention can be related to the measurable observed retention, and therefore, the reflection coefficient (σ) of the irreversible thermodynamic and Stefan-Maxwell models or the equivalent convection factor (W) of the hydrodynamic model can be readily calculated. It is interesting to note that only the convection factor (W) of the hydrodynamic model allows an estimation of the membrane pore directly as it is readily related to the geometrical structure of the membrane pore. The reflection coefficient can also be used, but assumption about the membrane pore geometry must be made following a hydrodynamic viewpoint. The hydrodynamic model is far more popular for membrane pore size characterisation and it will be used in this study to estimate the average pore size of several selected membranes. In the next section, a detailed mathematical model describing the transport phenomena of a sperical solute through a nanoporous membrane based on the hydrodynamic approach is developed.

Table 4.1: Comparison of the descriptive transport parameters of the three models (adapted from [180]).

	Thermodynamic term	Stefan-Maxwell term	Hydrodynamic term
Partitioning, steric			$\Phi=(1-\lambda)^2$ (for cylindrical pores)
Hindrance effect (friction, steric interactions)			K_c for convection K_d for diffusion
Combination effect for diffusion	Solute permeability, $P=D_{eff}/\delta$	D_2	Effective diffusion coefficient $D_{eff}=\Phi K_d$
Combination effect for convection	Reflection coefficient, σ	Reflection coefficient, σ where $D_2/D_1=1-\sigma$	$W=\Phi K_c$
Real retention	$R=\frac{\sigma[1-\exp(-Pe)]}{1-\sigma\exp(-Pe)}$	$R=\frac{(1-\frac{D_2}{D_1})[1-\exp(-Pe)]}{1-(1-\frac{D_2}{D_1})\exp(-Pe)}$	$R=\frac{(1-W)[1-\exp(-Pe)]}{1-(1-W)\exp(-Pe)}$

Pe is the membrane Peclet number.
See text for detail explanation and explanation of other symbols.

4. *Model development*

4.1 Solute Transport through a Nanoporous Membrane

The solute flux in a cylindrical pore can be expressed as the sum of diffusive and convective contributions [177, 197]:

$$J_s = -K^{-1}D_\infty \frac{\partial c}{\partial z} + GVc \qquad (4.13)$$

Here, J_s is the solute flux, V is the unperturbed fluid velocity, c is the solute concentration, D_∞ is the Stokes-Einstein diffusion coefficient, z is the axial position along the cylindrical pore, K is the enhanced drag, and G is the lag factor. The hydrodynamic coefficients K and G account for the finite pore size — the pore walls increase the drag on a solute molecule translating parallel to the pore axis ($K > 1$) and cause the velocity of the freely suspended solute to lag behind the approach velocity of the fluid ($G < 1$). Note that K and G depend on the ratio of the solute radius to pore radius, $\lambda = r_s/r_p$, as well as on the radial position in the pore, r, commonly expressed in terms of a dimensionless radial position, $\rho = r/r_p$.

The solute concentration c as well as the variables K, G, and V vary with the radial position ρ. Thus, one has to obtain the radial average solute flux, $\langle J_s \rangle$, by integrating over the pore cross section. The final result for the radial average solute flux at any axial position z is [177]:

$$\langle J_s \rangle = -K_d D_\infty \frac{d\langle c \rangle_z}{dz} + K_c \langle V \rangle \langle c \rangle_z \qquad (4.14)$$

The term $K_d D_\infty$ is known as the hindered diffusivity in the pore, while the term K_c accounts for the convective effects and may be considered as an effective drag factor.

We can now integrate the radial average solute flux over the entire pore length (or membrane thickness) L. To do this, the solute concentrations within the pore must be related to those outside the pore (in the bulk solution). This can be done using the distribution coefficient, Φ, for hard-sphere particles when only steric interactions are considered [177, 198]:

$$\Phi = \frac{\langle c \rangle_0}{c_0} = \frac{\langle c \rangle_L}{c_L} = (1-\lambda)^2 \qquad (4.15)$$

where c_0 and c_L are the solute concentrations just outside the pore entrance and pore exit, respectively, and $\langle c \rangle_0$ and $\langle c \rangle_L$ are the corresponding average concentrations just inside the pore at $z = 0$ and $z = L$, respectively. Thus, integration of Eq. 14.4 over the entire pore length (from $z = 0$ to $z = L$), with the boundary conditions from Eq. 4.15, yields the macroscopic solute flux equation:

$$\langle J_s \rangle = \frac{\Phi K_c \langle V \rangle c_0 \left[1 - (c_L / c_0)\exp(-Pe)\right]}{1 - \exp(-Pe)} \qquad (4.16)$$

where Pe is the membrane Peclet number, defined as

$$Pe = \frac{K_c \langle V \rangle L}{K_d D_\infty} = \frac{K_c \langle J_v \rangle L}{K_d \varepsilon D_\infty} \qquad (4.17)$$

In these equations, $\langle V \rangle$ is the radial average fluid velocity in a cylindrical membrane pore, which is equal to the membrane volumetric permeate flux, $\langle J_v \rangle$, divided by the membrane porosity, ε.

4.2 Solute Retention by Nanoporous Membranes

Relating the solute flux to the fluid velocity and the solute concentration in the permeate

$$\langle J_s \rangle = \langle V \rangle c_L, \qquad (4.18)$$

we can rearrange Eq. 16 to obtain the so-called sieving coefficient, S_a:

$$S_a = \frac{c_L}{c_0} = \frac{\Phi K_c}{\left[1 - \exp(-Pe)(1 - \Phi K_c)\right]} \qquad (4.19)$$

where c_0 and c_L are the solute concentrations just outside the pore entrance (i.e., on the membrane surface at the feed side) and pore exit (i.e., permeate side), respectively. The real (or intrinsic) retention is related to the sieving coefficient as

$$R_r = 1 - \frac{c_L}{c_0} = 1 - S_a = 1 - \frac{\Phi K_c}{1 - [1 - \Phi K_c]\exp(-Pe)} \qquad (4.20)$$

Note that the real retention, R_r, relates the solute permeate concentration to the membrane surface concentration, not the bulk feed concentration. The latter concentrations are different for solute rejecting membranes because of concentration polarization [199]. Using the film-theory for concentration polarization, it can be readily shown that the observed retention, R_o, is related to the real retention via

$$\ln\frac{1-R_r}{R_r} = \ln\frac{1-R_o}{R_o} - \frac{\langle J_v \rangle}{k_f} \qquad (4.21)$$

where k_f is the mass transfer coefficient. The determination of the mass transfer coefficient is described later in Materials and Methods. Note that in this equation, the observed retention, R_o, and the volumetric permeate flux, $\langle J_v \rangle$, are routinely measured during a typical nanofiltration experiment.

4.3 Determination of the Hydrodynamic Hindrance Coefficients

To use the above model to calculate solute retention by a nanoporous membrane, the hydrodynamic coefficients K_c and K_d must be determined. While various simplified theoretical expressions are available in the literature, most cover only a small range of λ, which limits their use to ultrafiltration and microfiltration membranes. The most complete expressions, which cover the entire range of λ, were given by Bungay and Brenner [177, 200]:

$$K_c = \frac{(2-\Phi)K_s}{2K_t} \qquad (4.22a)$$

$$K_d = \frac{6\pi}{K_t} \qquad (4.22b)$$

where

$$\begin{pmatrix} K_t \\ K_s \end{pmatrix} = \frac{9}{4}\pi^2\sqrt{2}(1-\lambda)^{-5/2}\left[1 + \sum_{n=1}^{2}\begin{pmatrix} a_n \\ b_n \end{pmatrix}(1-\lambda)^n\right] + \sum_{n=0}^{4}\begin{pmatrix} a_{n+3} \\ b_{n+3} \end{pmatrix}\lambda^n \qquad (4.23)$$

The coefficients a_n and b_n in this equation, for up to n = 7, can be found in the table below [200].

Table 4.2: Coefficients in K_t and K_s

N	a_n	b_n
1	−73/60	7/60
2	77293/50400	−2227/50400
3	−22.5083	4.0180
4	−5.6177	−3.9788
5	−0.3363	−1.9215
6	−1.216	4.392
7	1.647	5.006

Note that $H = \Phi K_d$ and $W = \Phi K_c$ are termed the hindrance factors for diffusion and convection, respectively. The dependence of these factors on the solute to pore radii ratio, λ ($=r_s/r_p$), calculated from Eqs. 4.15 and 4.22, is described in Figure 4.3. It is clearly shown that the finite pore size of porous membranes has a dramatic effect on solute diffusion and convection when λ is close to 1. This is quite relevant to nanofiltration membranes where the pore size is not much larger than the solute size.

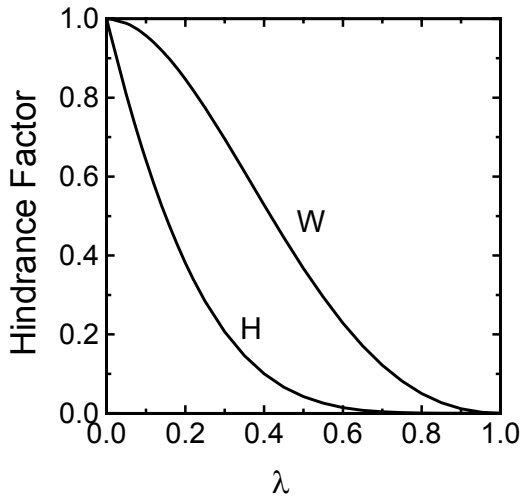


Figure 4.3: Dependence of hindrance factors for diffusion (H) and convection (W) of a neutral, spherical solute on the ratio of solute size to pore size, λ. The factors H and W were determined from Eqs. 4.15 and 4.22.

5. *Materials & Methods*

5.1 NF Membranes

Four NF membranes, denoted NF-270, NF-90 (FilmTec Corp., Minneapolis, MN), TFC-S and TFC-SR2 (Koch Membrane System, San Diego, CA) were used in this investigation. The membranes were received as flat sheets and were stored in deionized water at 4°C prior to experiments. As indicated by the manufacturer, the membranes consist of a semi-aromatic

piperazine based, polyamide layer on top of a microporous polysulfone support [144]. These membranes are negatively charged at pH levels above 3 (see Chapter 3). Sodium chloride retention by the TFC-SR2 is less than 10 % (at 1150 mg/L NaCl and 5 bar), while that of the TFC-S (at 1150 mg/L NaCl and 5 bar) is approximately 75%. Sodium chloride retentions by the NF-90 and NF-270 (at 3000 mg/L NaCl and 4.5 bar) are 85% and 40%, respectively.

5.2 Trace organic contaminants

Four radiolabeled steroid hormones, namely estradiol, estrone, progesterone, and testosterone were purchased from Sigma-Aldrich (Saint Louis, MO) and Perkin Elmer (Boston, MA) (see Chapter 3 for further details). The radiolabeled hormones were supplied in ethanol solution and were diluted with DI water prior to use. Specific radioactivity of estradiol, estrone, progesterone, and testosterone were 17, 65, 88, and 55 Ci/mmol, respectively. The stock solutions were stored in the dark at < 4°C. The purity of all hormones is higher than 97% at the time of purchase. Mass spectrospectry analysis (using a Finnigan LC/MS/MS) indicates that the purchased chemicals consist of both non-labeled and tritium labelled hormones. Experiments were completed within 5 months from the time of purchase. According to the manufacturers, it is estimated that the purity decreases approximately 2-5% each year, as these are unstable products.

Hormone mimicking compounds –nonyl phenol, bis phenol A, tert butyl phenol and pharmaceuticals –carbamazepine, sulfamethoxazole, and ibuprofen were purchased from Sigma-Aldrich (Saint Louis, MO). All of these chemicals are of analytical grade with minimum purity of 98 %. Radiolabeled hormones were analyzed using a Perkin Elmer scintillation counter (Tri-Carb 2900 TR) while hormone mimicking compounds and pharmaceuticals were analysed using a Shimadzu HPLC system as described previously in Chapter 3.

5.3 Organic Tracers

Low molecular weight, neutrally charged organic molecules — dioxane, erythritol, xylose, and dextrose — were chosen as organic tracers to characterize the average pore size of the NF membranes. These organic solutes are inert and do not adsorb to the membrane. Molecular weights, diffusivities, and Stokes radii of the selected organic tracers are listed in Table 4.3. A Shimadzu TOC analyzer (TOC V-CSH) was used to analyze the organic tracers. All organic tracers used were of analytical grade and were purchased from Fisher Scientific (Fair Lawn, NJ).

Table 4.3: Molecular Weight, Diffusivity, and Stokes Radius of Organic Tracers

Organic Tracer	Molecular Weight (g/mol)	Diffusivity [a] (10^{-10} m^2/s)	Stokes Radius [b] (nm)
Dioxane	88	9.1	0.234
Erythritol	120	8.1	0.263
Xylose	150	7.4	0.290
Dextrose	180	6.6	0.324

[a] Calculated using the Wilke and Chang equation [201] at 20° C

[b] Calculated using Stokes-Einstein equation

5.4 NF Membrane Test Unit

A laboratory-scale, crossflow membrane filtration test unit was used in this study. The unit consists of two identical plate-and-frame membrane cells, each housing a membrane coupon with an identical effective surface area of 7.7 × 3.0 cm. All test unit parts in contact with the solution are made of stainless steel or Teflon to minimize adsorption of the organic compounds used. Details of this NF membrane test unit (Yale cross flow system) are available in Chapter 3.

5.5 Membrane Filtration Protocol

Prior to each experiment, the membrane was stabilized at 12 bar (176.4 psi) using DI water for at least 16 hours until the permeate flux attained a constant value. The feed reservoir temperature was kept at 20±0.1°C throughout the experiment. Unless otherwise stated, permeate was recycled back to the feed reservoir.

To characterize the membrane pore size, a feed solution containing 20 mg/L (as TOC) of each organic tracer in DI water was used. The experiments were conducted at pressures of 4, 6, 8, 10 and 12 bar (58.8, 88.2, 117.6, 147.0, 176.4 psi) at a constant crossflow of 30.4 cm/s. After adjusting the pressure, the membrane filtration unit was run for 1 hour before taking samples for analysis.

After stabilizing the membrane (as described above), and prior to experiments with trace organic contaminants, DI water (4 L) was introduced to the feed reservoir. The cross flow and the permeate flux were adjusted to 30.4 cm/s and 15 μm/s (54 L/m^2h or 32.4 gfd), respectively. Natural hormones were then spiked into the feed reservoir to make up a concentration of 100 ng/L.

Similarly, hormone mimicking and pharmaceutically active compounds were spiked into the feed reservoir to make up a concentration of 500 μg/L. Feed and permeate samples (1 mL each) were taken for analysis at specified time intervals.

6. *Role of steric interactions in nanofiltration of trace organics*

6.1 Mass transfer coefficient measurement

The mass transfer coefficient, k_f, used in Eq. 4.9 (page 67), was determined experimentally using the method by Sutzkover *et al*. [196] as described earlier. As defined previously, the mass transfer coefficient ($k_f = D/\delta$) depends solely on the solute diffusivity and hydraulic condition of the experiment, which in turn only depends on the experimental system geometry and the cross flow velocity. Consequently, with a negligible permeate flux as is the case in this study, at a specified cross flow velocity, the filtration test unit would result in the same k_f value with all membranes.

Experiments were conducted at a cross flow velocity of 30.4 cm/s (corresponding to a channel Reynolds number of 3650) by first measuring the pure water flux, then adding NaCl to the feed reservoir to make up a feed salt concentration of 0.1 M and measuring the permeate flux and the permeate salt concentration. Knowing the permeate and feed salt concentrations and, thus, the corresponding osmotic pressures based on Van't Hoff equation, π_p and π_b, respectively, the applied pressure ΔP, the pure water flux J_w, and the permeate flux with the 0.1 M NaCl solution J_{salt}, enables the evaluation of the mass transfer coefficient or salt concentration at the membrane surface. This procedure was carried out at two different applied pressures, 6 and 10 bar (88 and 147 psi), and was repeated for the NF-270 and NF-90 membranes. The results are summarized in Table 4.4.

Table 4.4: Mass transfer coefficient of NaCl at a cross flow velocity of 30.4 cm/s

Membrane	Applied pressure (bar)	Pure water flux (μm/s)	Permeate flux of the NaCl solution (μm/s)	k_f (m/s)
NF-270	10.0	34.34	23.70	5.16E-05
NF-90	10.0	33.70	12.72	6.26E-05
NF-90	6.0	12.72	3.88	5.89E-05
Average				5.77E-05

Table 4.5: Corrected mass transfer coefficient of organic tracers at a cross flow velocity of 30.4 cm/s. (Diffusivity of NaCl in water is taken as 1.5 x 10^{-9} m/s at 20^{o}C)

Organic tracers	Diffusion coefficient (m^2/s)	Corrected k_f (m/s)
Ethylen Glycol	1.18E-09	4.55E-05
Dioxane	9.82E-10	3.78E-05
Erythritol	8.26E-10	3.18E-05
Xylose	7.40E-10	2.85E-05
Dextrose	6.72E-10	2.58E-05

The results obtained from different membranes at different applied pressures appear to be consistent with a standard deviation within 9.7 % of the average k_f value. This average value is used to determine the mass transfer coefficient of each of the organic tracers taking into account their diffusivity difference against that of sodium chloride as presented in Table 4.5. These mass transfer coefficients are then used to obtain real retention from observed retention following a thin film theory as described previously in Eq. 4.9 (page 67).

6.2 Estimation of NF Membrane Pore Size

Organic tracer real retention, R_r, was obtained from observed retention, R_o, after taking into account concentration polarization effects using Eq 4.9 and the measured mass transfer coefficient (see Table 4.5). Solute concentration polarization was quite severe at high permeate fluxes as indicated by the calculated ratio of solute membrane surface concentration to feed concentration; this ratio varied from 1.0 to 3.3 as the permeate flux increased from 12 to 45 μm/s. Real retentions of the organic tracers by the 4 selected membranes at different permeate fluxes (or transmembrane pressures) are summarized in Figure 4.4.

The selection of organic tracers appears to be justified, as organic tracers larger than dextran would result in a very high real retention, which may entail substantial errors. It is noted that observed retention of xylose by the NF-90 membrane is more than 90 %, corresponding to 97 % real retention. It is also noteworthy that the model replicates experimental data very well in all cases as can be seen in Figure 4.4.

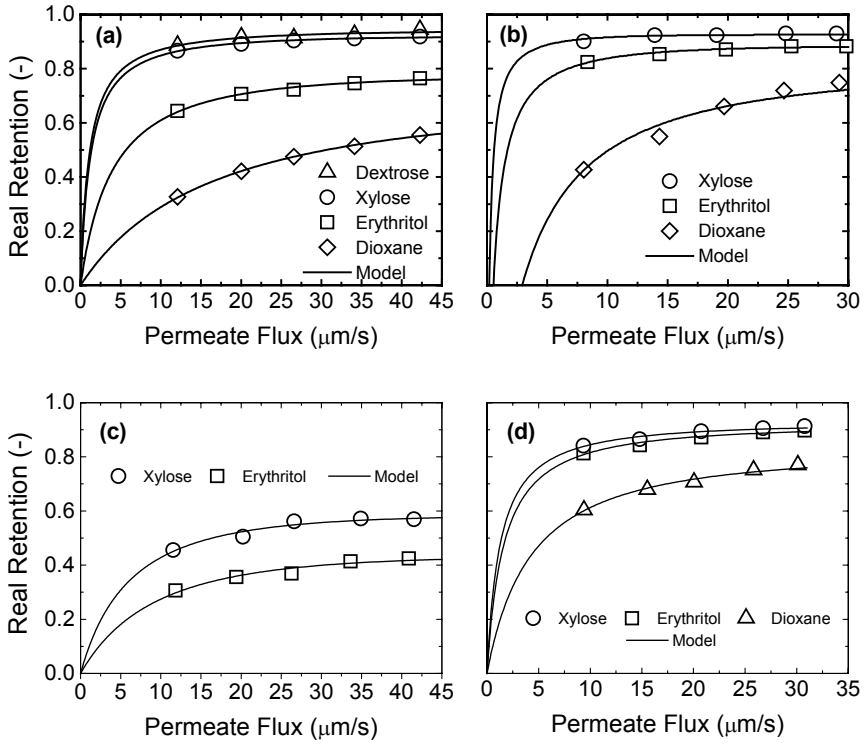


Figure 4.4: Real retention of the organic solute tracers as a function of permeate water flux for (a) NF-270 membrane, (b) NF-90 membrane, (c) TFC-SR2 membrane, and (d) TFC-S membrane. The symbols represent experimental data for the indicated organic solute tracers, while the solid lines represent the pore transport model predictions with the optimized parameters listed in Table 4.3. Feed solution contained 20 mg/L of organic tracer (as TOC) in deionized water. Other experimental conditions were as follows: crossflow velocity = 30.4 cm/s, pH ≈ 6.0, and temperature = 20.0°C. The permeate flux was varied by changing the applied pressure.

The obtained real retentions were used to estimate the NF membrane average pore size using the membrane pore transport model presented earlier. Since the model parameters ΦK_c and $Pe/\langle J_v \rangle$ $(= K_c L / \varepsilon D_\infty K_d$ based on Eq. 4.17) are uniquely related to R_r, these parameters were determined by fitting the retention data to the model (Eq. 4.20, page 71) using an optimization procedure (Solver, Microsoft Excel). The parameters ΦK_c and $Pe/\langle J_v \rangle$ are solely a function of the variable λ (ratio of solute radius to membrane pore radius, r_s/r_p), and thus were used to obtain λ for each solute and membrane. With the determined value of λ and the given solute radius r_s, the membrane average pore radius was calculated for each organic tracer solute retention data as shown in Table 4.6.

Table 4.6: Nanofiltration Estimated Pore Radii Obtained from Organic Tracer Experiments.

Compound	r_s (nm)	$\lambda = r_s/r_p$	Pore Radius, r_p (nm)
NF-90 Membrane			
Xylose	0.290	0.826	0.35
Erythitol	0.263	0.784	0.34
Dioxane	0.234	0.689	0.34
	Average		**0.34 ± 0.1**
NF-270 Membrane			
Dextrose	0.324	0.787	0.41
Xylose	0.290	0.752	0.39
Erythitol	0.263	0.600	0.44
Dioxane	0.234	0.522	0.45
	Average		**0.42 ± 0.3**
TFC-SR2 Membrane			
Xylose	0.290	0.387	0.68
Erythitol	0.263	0.486	0.60
	Average		**0.64 ± 0.6**
TFC-S Membrane			
Xylose	0.290	0.609	0.38
Erythitol	0.263	0.739	0.36
Dioxane	0.234	0.757	0.38
	Average		**0.37 ± 0.3**

The obtained pore radii are consistent for the different organic tracers for all membranes. The membrane average pore radius is 0.34, 0.37, 0.42, and 0.64 nm for the NF-90, TFC-S, NF-270, and TFC-SR2 membranes, respectively. This is consistent with NaCl retention by these membranes (NaCl retentions by the NF-90, TFC-S, NF-270, and TFC-SR2 are 85 %, 75 %, 40 %, and 10 %, respectively), although in additional to the sieving mechanism, charge repulsion can also contribute to the separation of charge species such as NaCl. The results suggest that the NF-90 is a tight NF membrane, while the TFC-SR2 has a very open pore size. Previous experimental data estimating average pore radii for various NF membranes yielded comparable results [194, 202-204].

6.3 Modeling organic retention based on steric hindrance interactions

If the solute-membrane interaction is purely steric, the observed retention for a given membrane pore size and solute radius, can be modeled at any given pressure (or permeate flux) using the pore transport model presented earlier (page 70). Based on the average membrane pore radii in Table 2, the predicted observed retention of inert organic solutes by the NF-270, NF-90, TFC-SR2, and TFC-S membranes as a function of molecular weight is shown in Figure 4.5.

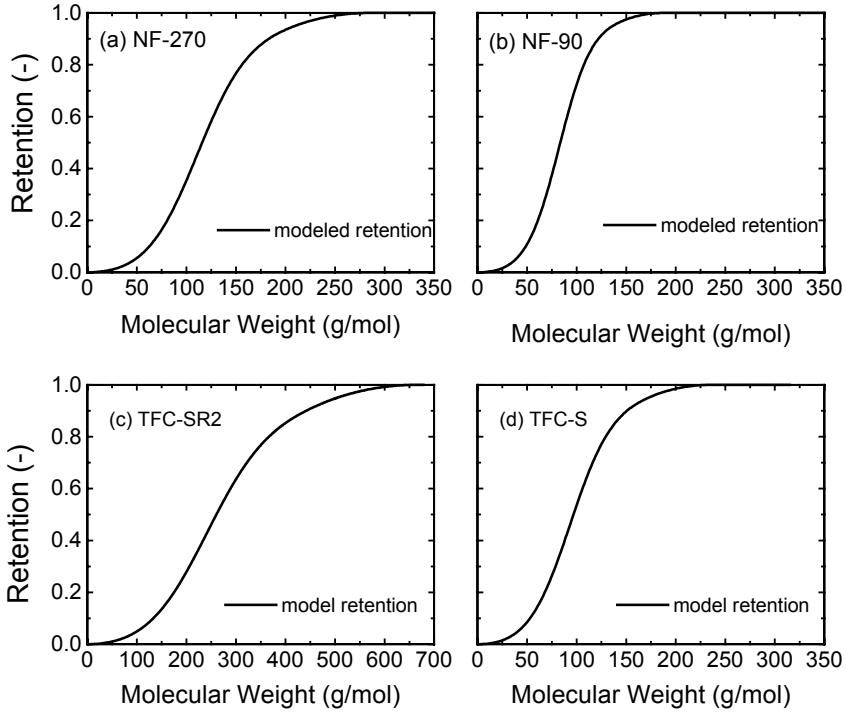


Figure 4.5: Model predictions for observed retention of non-adsorptive inert organics as a function of solute molecular weight based on the pore transport model for: (a) NF-270 membrane, (b) NF-90 membrane, (c) TFC-SR2 membrane, and (d) TFC-S membrane. The relevant organic tracer parameters in Table 4.3 were used in the model calculations. Other parameters used in modeling were as follows: cross flow velocity = 30.4 cm/s, permeate flux = 15 μm/s, and temperature = 20.0^{o}C.

The shape of the retention curve depends solely on the membrane average pore size. Retention curve of the NF-90 membrane is steepest as it has the smallest membrane pore size. In contrast, the TFC-SR2 membrane has a more gradual and wide retention curve due to its much larger pore size. It is noteworthy that these predicted retentions are only applicable to the same experimental condition used for organic tracers as described previously. However, they can serve as an excellent benchmark for the elucidation of the separation mechanisms by the membranes. If membrane filtration experiments of trace organic contaminants can be conducted with the same experimental condition, one could determine whether trace organic retention mechanism is governed by sieving mechanism, charge repulsion, or any other factors can contribute to the transport of such trace organics through the membranes. If the first case occurs, retention would coincide with the predicted line, whereas retention could be higher if charge repulsion also contributes to the separation process. The NF-270 and NF-90 membranes are selected for further study in order to examine these hypotheses. The results are presented in the next section. Further examination can also be found in the following chapter of this dissertation.

6.4 Nanofiltration of hormones and hormone mimicking compounds

Retention of organics by NF membranes can be attributed to a number of mechanisms, the most common of which are steric interaction (or size exclusion), charge exclusion or repulsion (see Chapter 5), and adsorption to the membrane surface (see Chapter 6). The natural hormones and hormone mimicking compounds investigated in this study are undissociated at the pH of the experiments (pH 6), and only polar moieties contribute to the charge distribution within the molecule. Under these conditions, ionic (charge) interactions between the hormones and the membranes are absent, and steric exclusion and adsorptive effects are expected to dominate.

Figures 6 to 9 present the concentration of estradiol, estrone, testosterone, and progesterone in the permeate and feed as a function of time following filtration by the NF-270 and NF-90 membranes. Because natural hormones can adsorb (or partition) to the membrane polymer, it is not surprising to observe the continual decrease in feed concentration over a relatively long period of time. The feed concentration then stabilizes as the adsorption of hormones to the membrane reaches equilibrium. This phenomenon is consistently observed for all natural hormones with both the NF-270 and NF-90 membranes.

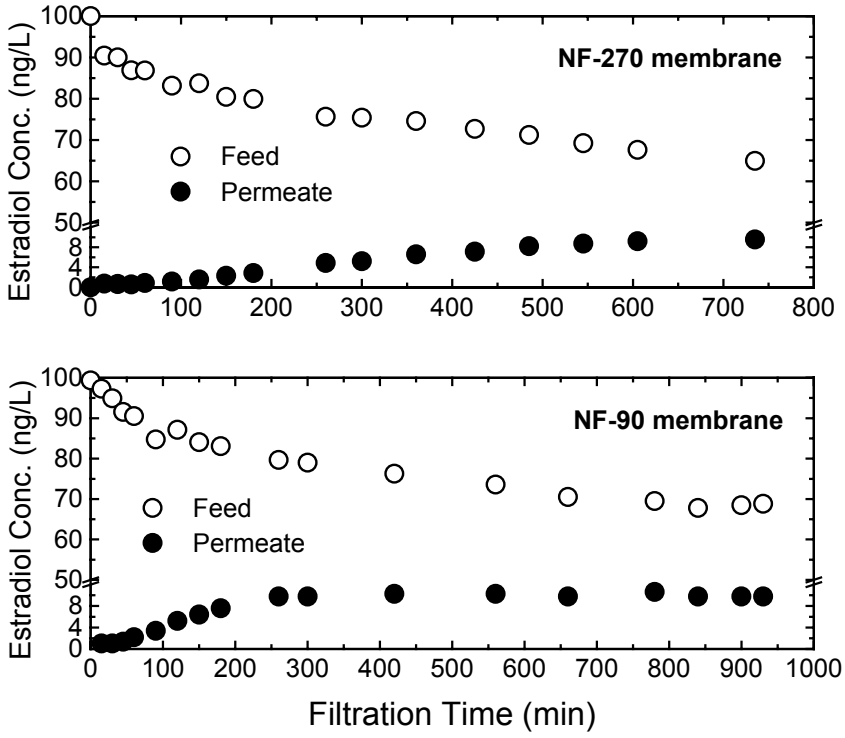


Figure 4.6: Permeate and feed concentrations of estradiol as a function of filtration time for the NF-270 membrane (top) and NF-90 membrane (bottom). The feed solution contained 100 ng/L estradiol in deionized water. Other experimental conditions were as follows: cross flow velocity = 30.4 cm/s, permeate flux = 15 μm/s (or 54 L/m.h), pH ≈ 6.0, and temperature = 20.0°C.

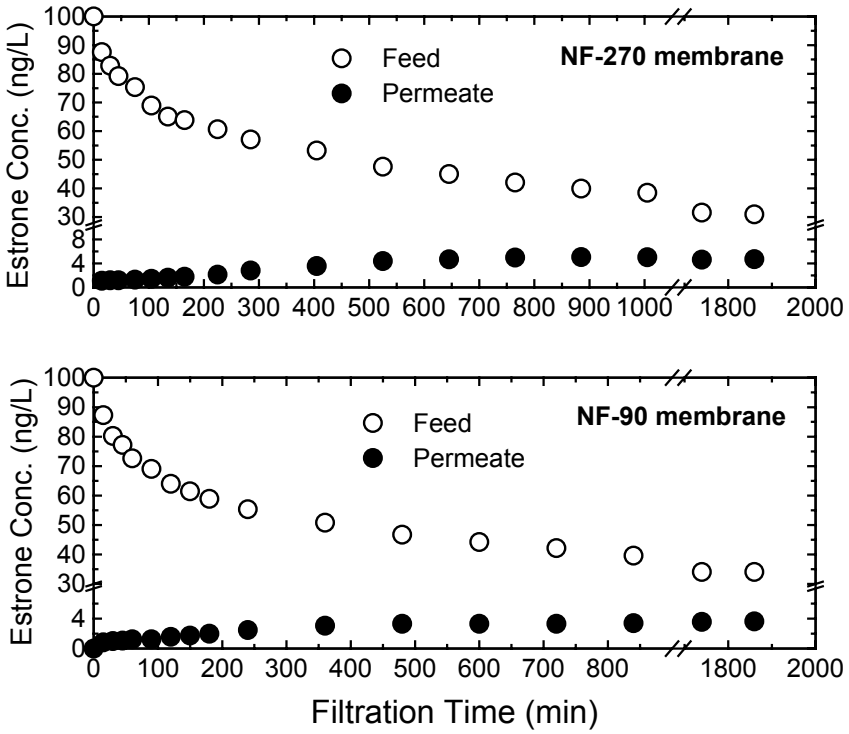


Figure 4.7: Permeate and feed concentrations of estrone as a function of filtration time for the NF-270 membrane (top) and NF-90 membrane (bottom). The feed solution contained 100 ng/L estrone in deionized water. Other experimental conditions were as Figure 4.6.

A similar set of experiments was also conducted for nonyl-phenol, bis phenol A, and tert butyl phenol. Concentration of hormone mimicking compound in the feed solution was however 500 μg/ so that accurate analysis using an HPLC system could be achieved. Concentration of bis phenol A and tert butyl phenol in the feed and permeate feed as a function of time following filtration by the NF-270 and NF-90 membranes is shown in Figure 4.10. Similar to the nanofiltration of steroid hormones, hormone mimicking compounds also adsorb (or partition) to the membrane to a considerable extent. The adsorption of the trace organic hormones and hormone mimicking compounds will be described in further detail in Chapter 6. Adsorption of nonyl phenol to both the NF-270 and the NF-90 membranes is so significant that at the end of the experiment nonyl phenol is completely depleted from the feed solution. Consequently, experimental data for this compound has been excluded.

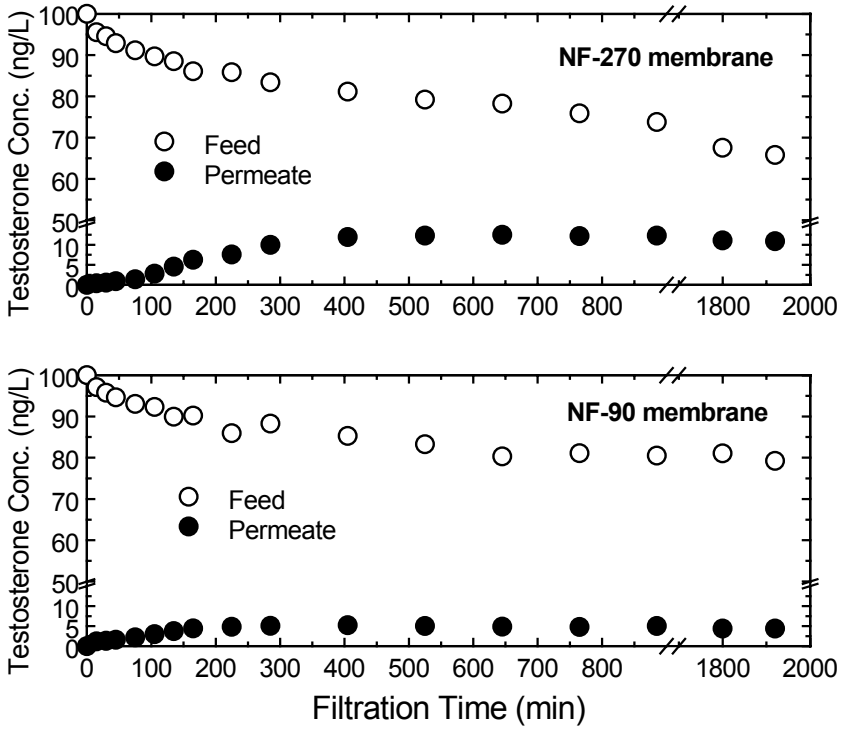


Figure 4.8: Permeate and feed concentrations of testosterone as a function of filtration time for the NF-270 membrane (top) and NF-90 membrane (bottom). The feed solution contained 100 ng/L testosterone in deionized water. Other experimental conditions were as Figure 4.6.

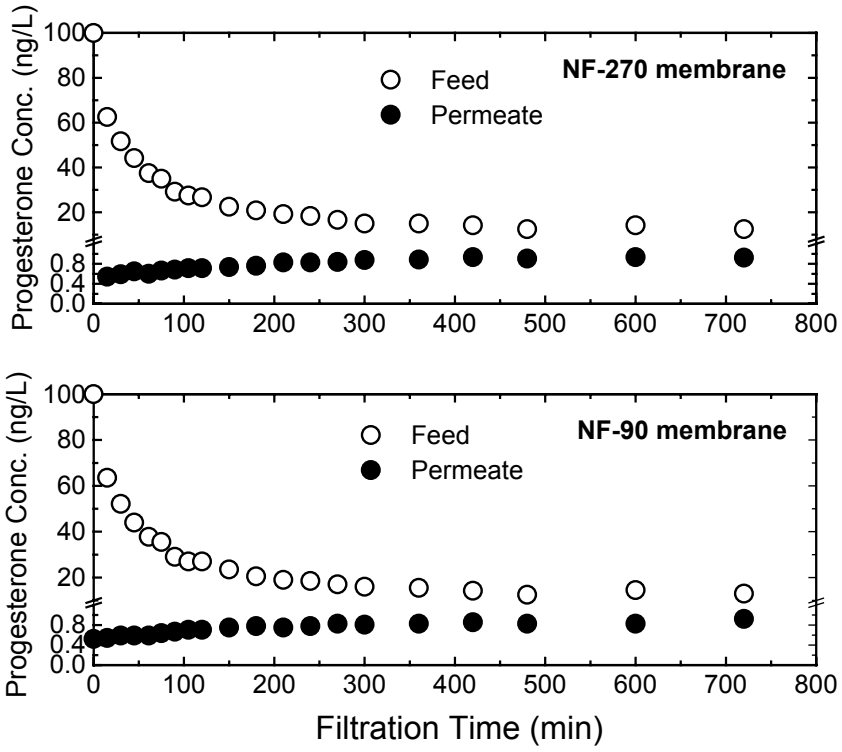


Figure 4.9: Permeate and feed concentrations of progesterone as a function of filtration time for the NF-270 membrane (top) and NF-90 membrane (bottom). The feed solution contained 100 ng/L progesterone in deionized water. Other experimental conditions were as Figure 4.6.

The molecular weights of the natural hormones range from 270 to 315 g/mol (see chapter 3), which translates to Stokes radius in the range from 0.4 to 0.5 nm (radius of equivalent sphere) using the Wilke and Chang and the Stokes-Einstein equations [201]. This is larger than the average pore radius of the NF-270 and NF-90 membranes. Thus, one would expect the retention of the hormones to be nearly complete. When converting the feed and permeate concentration relationship (Figures 6-9), into observed retention (Figure 4.11), it appears that retention of the natural hormones is initially high, almost 100%. However, as pointed out earlier, this initially high retention is attributed to adsorption of natural hormones to the membrane polymer. The retention decreases continuously as hormone adsorption onto the polymeric membranes progresses, and eventually stabilizes when equilibrium is achieved.

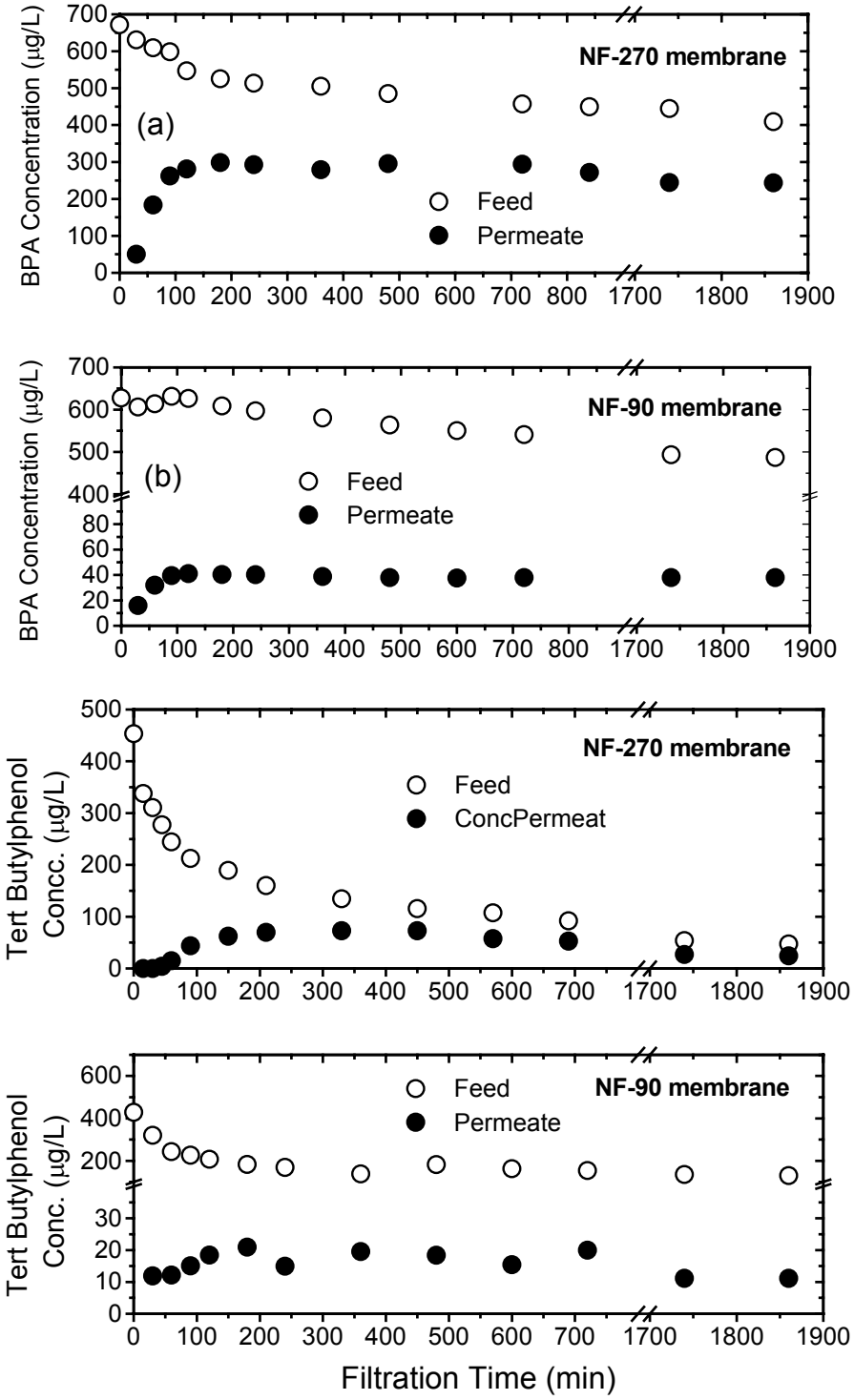


Figure 4.10: Permeate and feed concentrations of bis phenol A as a function of filtration time for (a) the NF-270 membrane, (b) the NF-90 membrane and of tert butylphenol for (c) the NF-270 membrane, (d) the NF-90 membrane. The feed solution contained approximately 500 μg/L of the corresponding hormone mimicking compound in deionized water. Other experimental conditions were as Figure 4.6.

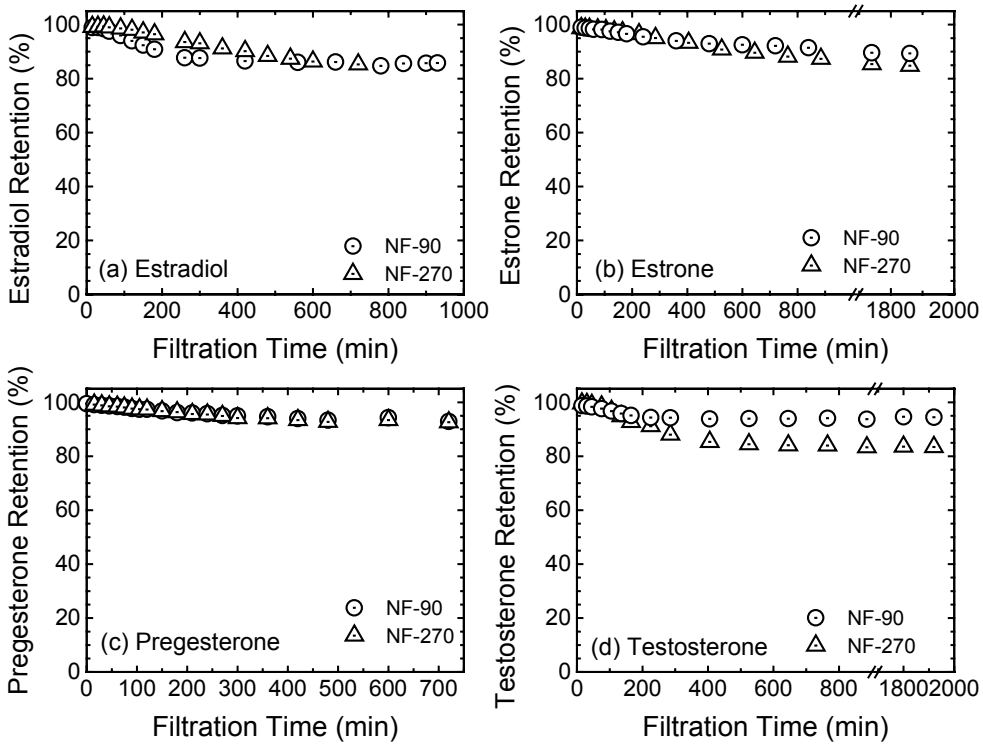


Figure 4.11: Retention of (a) estradiol, (b) estrone, (c) progesterone, and (d) testosterone by the NF-270 and NF-90 membranes as a function of time. The feed solution contained 100 ng/L of the corresponding hormone in deionized water. Other experimental conditions were as Figure 4.6.

The permeate concentration of natural hormones (Figures 6-9) follows a characteristic breakthrough curve as often observed in activated carbon packed-column adsorption. However, the breakthrough concentrations are small — ranging from less than 1 ng/L for progesterone to less than 10 ng/L for estradiol — indicating that size exclusion is still a significant retention mechanism when adsorption has reached equilibrium. This observation is more evident when examining the hormone mimicking compounds in this study. Bis phenol A (MW 228 g/mol) and tert butylphenol (MW 150 g/mol) are both considerably smaller than the pore size of the NF-270 membrane. Consequently, retention of approximately 50% can be observed for both membranes at equilibrium (see Figure 4.12). It is however, interesting to note that these two compounds have almost the same retention despite the fact that they have significantly different molecular weights (and molecular sizes).

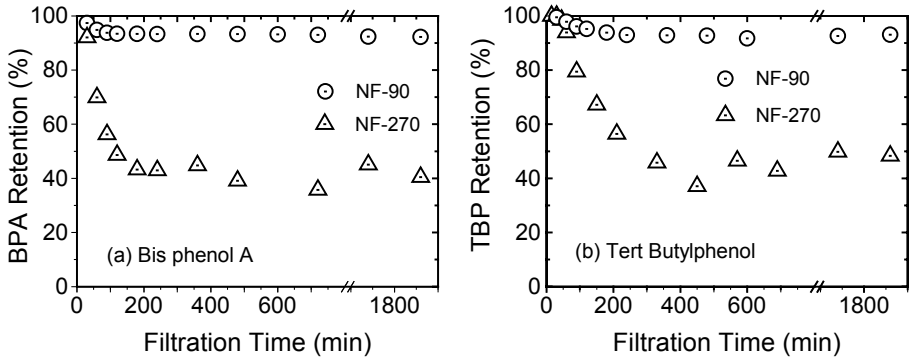


Figure 4.12: Retention of (a) Bis phenol A and (b) Tert Butylphenol by the NF-270 and NF-90 membranes as a function of time. The feed solution contained approximately 500 μg/L of the corresponding hormone mimicking compound in deionized water. Other experimental conditions were as Figure 4.6.

From observations of both steroid hormones and hormone mimicking compounds, it appears that due to adsorption of these compounds to the membrane, retention is lower, as predicted based solely on the steric interaction mechanism. This observation supports the hypothesis that there is an additional transport mechanism of natural steroid hormones and hormone mimicking compounds, namely partitioning and subsequent diffusion across the membrane, as we discuss in detail later in Chapter 7.

6.5 Nanofiltration of pharmaceutically active compounds

Because carbamazepine is a base, at a pH lower than its pK_a value of 2.3, it can undergo the protonation process, as the compound's triamine functional group receives a proton and thus a positive charge. Above this pH, the compound remains a neutral species. Concentration of carbamazepine in the feed and permeate as a function of time following filtration by the NF-270 and NF-90 membranes is shown in Figure 4.13. In contrast to steroid hormones and hormone mimicking compounds, carbamazepine does not adsorb to the membrane and the feed concentration appears constant throughout the experiments. This is possibly because of their relatively small log K_{ow}, attributed to its polar functional groups as can be seen from the molecular structure (see Chapter 3). Correspondingly, retention is constant over time, as sorption-diffusion does not occur in this instance.

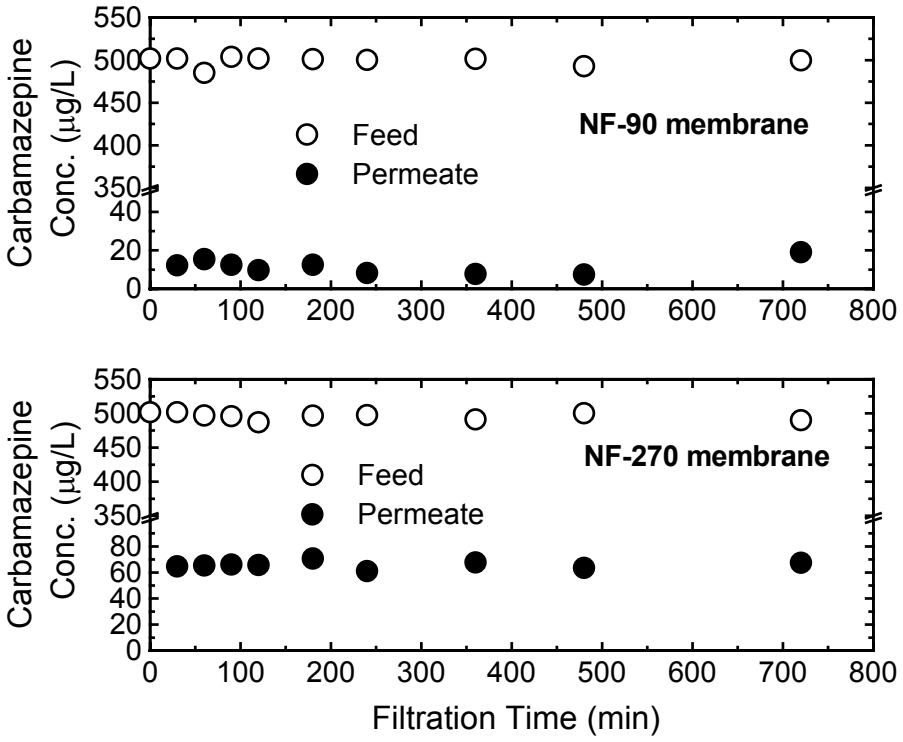


Figure 4.13: Permeate and feed concentrations of carbamazepine as a function of filtration time for the NF-90 membrane (top) and NF-270 membrane (bottom). The feed solution contained 500 μg/L carbamazepine in deionized water. Other experimental conditions were as Figure 4.6.

Carbamazepine retention appears to be considerably higher than that of steroid hormones and hormone mimicking compounds, although they are comparable in molecular weight. Retention by the NF-90 membrane is 98.5 % while that of the loose NF-270 membrane is approximately 87 %. It is noteworthy that carbamazepine retention by the NF-270 membrane is slightly lower than retention of charged PhACs such as sulfamethoxazole (99 %) and ibuprofen (96 %) by the same membrane in an identical experiment condition. Retention of charged organics will be examined in detail in the next chapter.

6.6 Trace organic removal mechanisms

Hormone and hormone mimicking compound adsorption to the membrane is the predominant removal mechanism at the initial stage of filtration. Detailed analysis of the adsorption phenomenon is presented in Chapter 6 of this dissertation. At a later state, retention of natural hormones and hormone mimicking compound is lower than expected based purely on a steric or sieving mechanism.

Although size exclusion is the major separation mechanism at the later stages of filtration, it is proposed that partitioning and subsequent diffusion through the membrane polymer matrix results in a somewhat lower retention. In this process, the adsorption of natural hormones onto the membrane skin layer should be fast and, thus, not a rate-limiting step. Rather, the rate of steroid hormone transport across the membrane is governed by the diffusion through the skin (active) layer of the thin-film composite NF membranes. A recent study suggests that the polyamide skin layer of the NF-270 is very thin, in the range of 15 to 40 nm, compared to 200 - 300 nm for most RO membranes [144, 145]. Thus, although diffusive transport of steroid hormones and hormone mimicking compounds through the membrane polymeric matrix is slow, a small but clear deviation of retention from the theoretical retention curve based on size exclusion is observed (Figure 4.14). This is more obvious for the "loose" NF-270 membrane, which retained significantly less tert butylphenol and bis phenol A as compared to the predicted retention curve based solely on steric interactions. The diffusion process of trace organic through the membrane skin layer is further examined in Chapter 7.

Measured retentions of both neutral and negatively charged pharmaceuticals were also included in Figure 4.14 for comparison purposes, although the nanofiltration of pharmaceuticals will be delineated in much more detail in the next chapter. Figure 4.14 indicates that charge repulsion can result in a higher retention as compared to the predicted curve based solely on steric interactions. It is possible that the evidence could be much clearer if smaller organic solutes were selected. Complete removal efficiency can be achieved for the negatively charged species of both ibuprofen and sulfamethoxazole by the "tight" NF-90 membrane, whereas retention of the negatively charged ibuprofen by the "loose" NF-270 is marginally higher than the predicted curve.

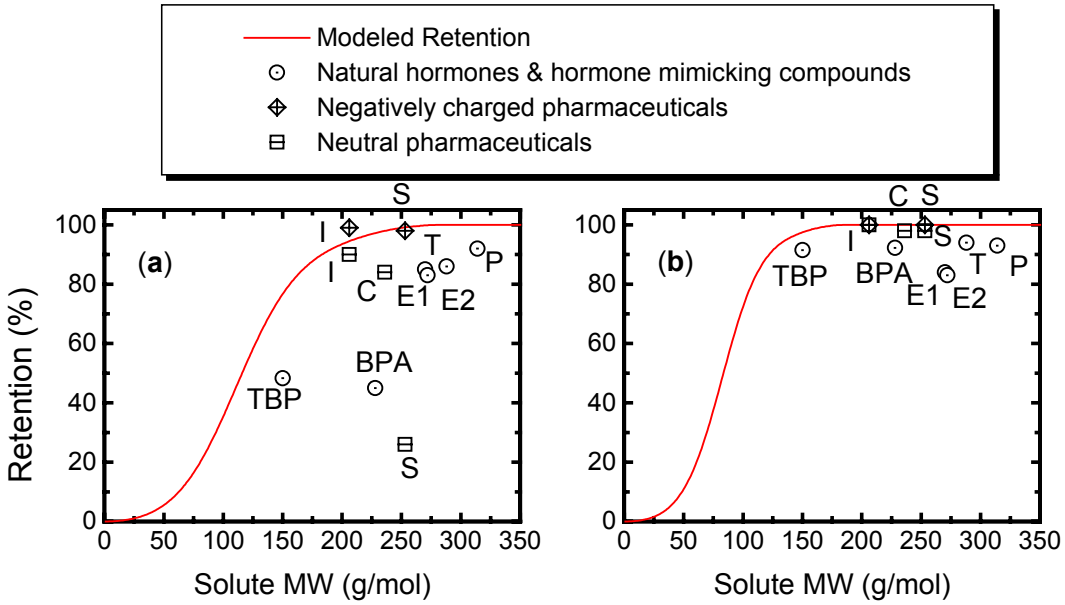


Figure 4.14: Model predictions for observed retention by the (a) NF-270 and (b) NF-90 membranes as presented previously in Figure 4.5. Also included are the measured observed retentions of the four hormones and two hormone mimicking compounds (circle symbols): E1 - estrone, E2 - estradiol, T - testosterone, P – progesterone, BPA – bisphenol A, and TBP – tert butylphenol; three neutral pharmaceuticals (diamond symbols) and two negatively charged pharmaceutically active compounds (diamond symbols): C – carbamazepine, I – ibuprofen, and S - sulfamethoxazole. The observed retention of the steroid hormones and hormone mimicking compounds was taken at the end of the adsorption stage (after 12 hours). Other parameters used in modeling were as Figure 4.6.

In the absence of any electrostatic repulsion, the influence of the compound specific physicochemical properties also becomes more prevalent in the case of the two non-adsorptive pharmaceuticals carbamazepine and sulfamethoxazole. It is striking to note that retention of the neutral species of sulfamethoxazole is significantly lower than that of carbamazepine (Figure 4.14) despite the fact that molecular weight sulfamethoxazole is higher than that of carbamazepine (see Chapter 3). The phenomenon can be explained following an argument by Bruggen *et al.* [126], who reported that molecules with high dipole moments (above 3 Debye) might show a lower retention than molecules with approximately the same molecular weight but with a lower dipole moment. Because of the electrostatic attraction between polar moieties of the molecule with the membrane fixed charged groups, the dipole is directed towards the membrane pore in an orientated instead of a random fashion. This does not result in a static but rather statistical tendency of the fast moving molecules to approach the membrane pore head on. The effect is apparent when comparing the three-dimensional models of sulfamethoxazole to carbamazepine (see Chapter 3). The sulfamethoxazole molecule is long and cylindrical in shape with its dipole moment distributed

along the main axis. By contrast, carbamazepine is more bulky in shape with no clear dimensional features. In addition, the dipole moment of sulfamethoxazole is 5.4 Debye, significantly higher than that of carbamazepine, which is 3.6 Debye. Nevertheless, interactions responsible for separation remain steric in nature. Because average pore radius of the NF-90 membrane is substantially smaller than the pharmaceuticals in this study, no polarity effects can be observed with this tight NF-90 membrane (see Figure 4.14).

It is clear from Figure 4.14 that adsorption, possibly followed by diffusion, charge interaction, and in the case of high dipole moment compounds polar interaction, can influence the separation process of trace organics by NF membranes. However, for uncharged organics, steric interaction retains its primary role as a dominant removal mechanism in the long term. It appears that the analysis and results in this chapter can be used to explain why retention of organic solutes can be correlated well with their molecular weight (or size) in some cases [64, 122, 205] whereas very scattered data is observed in others [13, 134, 205].

7. *Conclusions*

Steric interaction is a major removal mechanism in membrane filtration processes. Many great efforts have been devoted to study and develop membrane pore size characterisation techniques. As reviewed in this chapter, although many techniques are available, only solute reference transport method appears suitable for the study of NF membranes. It has also been revealed that three different approaches- namely irreversible thermodynamic, Stefan Maxwell, and hydrodynamic methods can be used to develop a model for pore size characterisation. In fact they would produce analogous equations in their final form. Since the hydrodynamic approach appears consistent with physical explanation and has been widely used by membrane scientists, it was used in this chapter to develop a steric hindrance transport model for membrane pore size characterisation.

The developed model produces consistent results with various reference organic tracers. Based on these average pore radii values, predicted retention curves based solely on steric interaction can be established and used to elucidate trace organic removal mechanisms.

It appears that adsorption is the dominant removal mechanism for steroid hormones and hormone mimicking compounds at the initial filtration stage. At the later stage, retention of natural hormones and hormone mimicking compounds is lower than expected based purely on a steric or sieving mechanism. In contrast, pharmaceutically active compounds with low hydrophobicity do not

adsorb to the membrane. Charge repulsion also enhances retention and results in marginally higher retention than compared to the predicted curve, again based solely on steric interaction. It can be concluded that although adsorption followed by diffusion and charge interaction can influence the separation process, steric interaction remains the most important removal mechanism. For compounds that have a high dipole moment and are cylindrical in shape, polarity influence can be quite significant. However, interaction responsible for separation remains steric in nature.

Chapter 5

Charge interaction

1. *Introduction*

Electrostatic interactions between the membrane charged surface and anionic solutes have probably become an inherent characteristic of nanofiltration membrane throughout its development history. Given the significance of electrostatic interaction in NF membrane filtration processes, an enormous amount of dedicated research work has been devoted to this topic, see for example [123, 130, 133, 148, 156, 193, 194, 206]. Numerous models have to date been proposed for anionic solutes. The majority of such models are also based on the fundamental irreversible thermodynamic principle pioneered by Spiegler and Kedem [186, 187], or the well known hydrodynamic principle mentioned previously in Chapter 4 with an addition of the charge repulsion effect. They are in fact indispensable in a mechanistic elucidation of numerous phenomena observed in a NF membrane filtration process involved charged solutes. However, it is remarkable that such a model has to date not been applied to investigate the separation process of anionic trace organics in membrane filtration processes and to relate various solution chemistry, solute properties, and membrane characteristics to the retention of such contaminants by NF membranes. Little is known about the influence of such factors on charge repulsion as well as its role in the retention of charged trace organic contaminants.

This chapter examines charge interaction as a removal mechanism of ionisable trace organics by NF membranes. A mathematical model has been developed and used to theoretically investigate the potential effects of the solution chemistries (pH and ionic strength), membrane properties (average pore size and membrane surface charge density) and retention of charged solutes. Such theoretical findings were then confirmed by experimental data conducted using a cross flow NF membrane filtration test unit. Retention of a steroid hormone, a hormone mimicking compound, and two pharmaceuticals in their anionic form was related to the membrane and solute physicochemical properties, and factors influencing electrostatic interaction were lineated and discussed.

2. *Theory*

2.1 Electrostatic interaction on surfaces

Most (if not all) NF/RO membranes carry fixed charged groups and the membrane surface or pore wall can be considered as a charged surface. Inherently, there are electrostatic interactions between charged solutes and the membrane surface. Such interactions lead to a very important phenomenon known as Donnan exclusion (see Chapter 2), frequently mentioned in the desalting and softening processes using NF/RO membranes. Electrostatic interaction is not confined to the field of membrane filtration, it is indeed an important phenomenon in aquatic chemistry. Basic theories describing the nature of such interactions have been well developed and an analytical solution was derived at the beginning of the previous century by some of the most renowned physiologists including Gouy, Chapman, Debye, and Hückel [207, 208]. A simplified mathematical solution is summarised here to fundamentally signify their implications towards NF/RO membrane filtration processes. Detailed discussion and mathematical derivation of these theories can be found in comprehensive aquatic chemistry texts, such as the one written by Morel and Hering [208].

For simplicity, we consider an infinite charged surface immersed in a 1:1 (NaCl) electrolyte solution. The one-dimensional Poisson-Boltzmann equation can be written as [208]:

$$\frac{d^2\Psi}{dx^2} = \frac{-FI}{\varepsilon\varepsilon_0}\left(e^{-F\Psi/RT} - e^{+F\Psi/RT}\right) \qquad (5.1)$$

where ψ is the electro potential of the surface. F, R, and I are the Faraday constant, gas constant, and the ionic strength of the bulk solution, respectively. ε is the relative dielectric constant of water, ε_0 is the permittivity of vacuum, and x is the distance from the charged surface.

Integrating this equation after multiplying both sides by $2d\Psi/dx$ with the boundary condition $\Psi = d\Psi/dx = 0$ when x=∞ (in other word, electro potential of the charged surface is zero in the bulk solution), we have:

$$\left(\frac{d\Psi}{dx}\right)^2 = -\frac{2FI}{\varepsilon\varepsilon_0}\frac{RT}{F}\left(2 - e^{-F\Psi/RT} - e^{+F\Psi/RT}\right) = \frac{8RT}{\varepsilon\varepsilon_0} I \cdot \sinh^2\frac{F\Psi}{2RT} \qquad (5.2)$$

Take the square root (with the necessary negative sign to indicate the direction of the electro potential) we obtain:

$$\frac{d\Psi}{dx} = -\left(\frac{8RTI}{\varepsilon\varepsilon_0}\right)^2 \sinh\ \frac{F\Psi}{2RT} \tag{5.3}$$

With the boundary condition $\psi=\psi_0$ at x=0 and $\psi=0$ at x=∞, one can further solve Eq. 5.3 to get a quite complicated solution. Again for simplicity, we assume a small potential ($F\Psi / RT < 1$), which is usually correct for polymeric NF/RO membranes in dilute electrolyte solution. In consequence, a much more simplified solution is obtained:

$$\Psi = \Psi_0 e^{-\kappa x} \tag{5.4}$$

where:

$$\kappa^2 = 2\frac{F^2}{\varepsilon\varepsilon_0 RT} I \tag{5.5}$$

or for an aqueous solution:

$$\frac{1}{\kappa} = 0.30 \cdot I^{-1/2} \tag{5.6}$$

The Debye length (1/κ) is a characteristic distance (with the unit of nm). It is also known as the double layer thickness, a very important parameter in many models describing the transport and separation processes of ionic solutes in NF/RO membranes. As can be seen in Eq. 5.4, at a distance of 1/κ (which is the Debye length), the electrical potential has been decreased to a value of e (κ/κ=1/e=0.37). Physical significance of the Debye length is demonstrated in Figure 5.1.

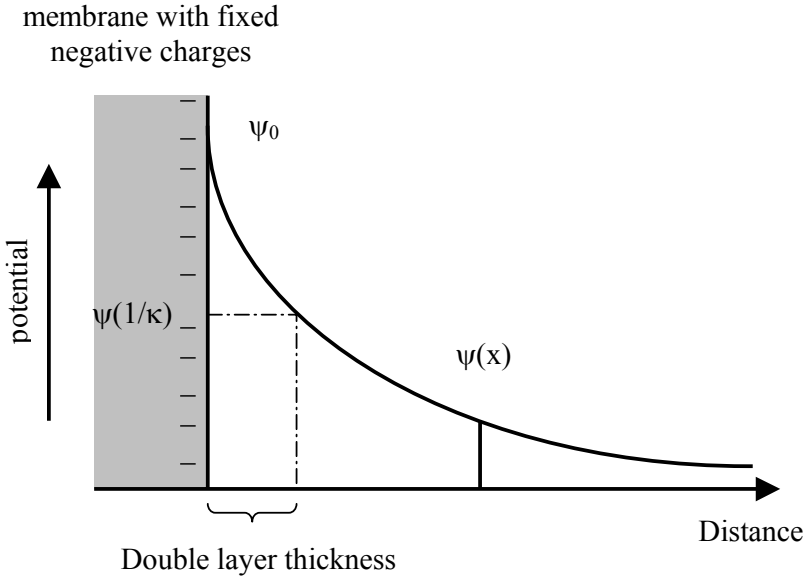


Figure 5.1: Representation of the electrical potential as a function of distance following Eq. 5.4.

Qualitatively, Figure 5.1 clearly illustrates the dependency of charge interaction on the Debye length, which in turn is a function of the solution ionic strength. Strong charge interaction is expected for a solution with a weak ionic strength, corresponding to a large Debye length. On the other hand, a high ionic strength (the Debye length approaches zero) can diminish the effect of charge interaction. In fact, the Debye length is an important parameter of any mathematical model for the separation of ionic species in NF/RO membrane filtration processes. We will utilise one such model to quantitatively re-examine this premise in the following section.

2.2 Transport of charged solute through a nanoporous membrane

Taking a similar approach as described in Chapter 4 with the addition of the electrical interaction term, assuming ideal conditions, solute flux through a cylindrical pore can be written as:

$$J_i = J_{i,diff} + J_{i,conv} + J_{i,elec} \tag{5.7}$$

This is the basis of a well known "extended Nernst-Planck" equation, often mentioned in membrane texts. In absence of coupling phenomena, the Nernst-Planck equation can be given as:

$$J_i = -D_{si}\frac{dc_i}{dx} + c_i J_v - \frac{z_i F c_i D_{si}}{RT}\frac{d\Psi}{dx} \tag{5.8}$$

The last term of the right hand side represents charge interaction between ionic solute and the membrane charged surface. For a simplified 1:1 electrolyte solution containing NaCl for example, the total volume flux, solute flux $J_1 + J_2$ (for Na^+ and Cl^-), and electric current I_{cur} can be obtained by integrating each flux over the cross section area of the membrane pore as follows:

$$< J_v > \;=\; \frac{2}{r_p^{\,2}}\int_0^{r_p} v_x\, dr \tag{5.9}$$

$$< J_1 + J_2 > \;=\; \frac{2}{r_p^{\,2}}\int_0^{r_p} (j_1 + j_2)\, dr \tag{5.10}$$

$$< I_{cur} > \;=\; \frac{2F}{r_p^{\,2}}\int_0^{r_p} (j_1 + j_2)\, dr \tag{5.11}$$

where r_p is the membrane pore radii. It is noted that the solvent velocity (v_x) is a function of the effective pressure and electrical potential, which implicitly includes the Debye length [129].

Eqs. 5.9 to 5.11 form the so-called space charge (SC) or Donnan Steric Pore model, which has been used quite extensively for nanofiltration membranes. At a steady stage, assuming no electric current

conditions (i.e. $<I_{cur}>=0$), one can numerically solve the equation system of Eqs. 5.9-5.11 to obtain solute retention at a specified condition, as have been demonstrated by several influential researchers in this area such as Wang, Nakao, Bowen, and Welfoot [129, 193, 194]. However, such a numerical procedure is complicated and most of all it cannot be used to explicitly describe the relationship between retention and the solution chemistries (namely ionic strength) or the membrane characteristics (such as pore size and surface charge density). Therefore, it is necessary for further refinement to exquisitely illustrate such a relationship. This can be done by taking advantage of some simplified assumptions.

2.3 Teorell-Mayer-Sievers (TMS) model

The SC model described above takes into account ion concentration and electric potential distribution in the radial direction of the membrane pore. However, one can assume that both parameters are uniform as the primary concern is with the axial transport along the membrane pore. With these assumptions, the calculation is much simpler. This is called the TMS model, as it was named after three physiologists Teorell, Mayer, and Sievers [206].

Again with the extended Nernst-Planck equation as described previously:

$$J_i = -D_i \frac{dc_i}{dx} + c_i J_v - \frac{z_i F c_i D_i}{RT} \frac{d\Psi}{dx} \tag{5.12}$$

Due to electroneutrality within the membrane and in the external solution, the following expressions can be obtained:

$$\sum_i (z_i c_{i,m}) - X = 0 \text{ (inside the membranes)} \tag{5.13}$$

$$\sum_i (z_i c_i) = 0 \text{ (external solution)} \tag{5.14}$$

Where X is the membrane volume charge density and z is the electro chemical valence of the ion (for a simplified case with NaCl, z=1 for both Na^+ and Cl^-). At the interface between the membrane and external solution, there exists a Donnan equilibrium, which can be expressed as:

$$\Psi_{don} = \frac{RT}{z_i F} \ln\left(\frac{c_{i,m}}{c_i}\right) \tag{5.15}$$

At steady state, assuming a no electrical current condition, we have:

$$I = \sum_i (z_i J_i) = 0 \tag{5.16}$$

For a simplified case with 1:1 electrolyte background solution (of NaCl for example), we have $J_1=J_2=J_s$. Combining Eqs. 5.16 and 5.12, the solute flux can be expressed as:

$$J_s = -\frac{D_1 c_{1,m} D_2 c_{2,m}}{D_1 c_{1,m} + D_2 c_{2,m}} \frac{d}{dx} \ln(c_{1,m} c_{2,m}) + \frac{D_1 + D_2}{D_1 c_{1,m} + D_2 c_{2,m}} c_{1,m} c_{2,m} J_v \quad (5.17)$$

Integrating Eq. 5.17 across the membrane thickness with the boundary conditions of Eqs. 5.13-5.15 we can get:

$$\frac{J_v L}{D_s} = -\frac{1}{2}\left[\ln \frac{Z(c_p)^2 - 2c_p Z(c_p) + A}{Z(c_0)^2 + 2c_p Z(c_0) + A} + \frac{c_p}{B} \ln \frac{Z(c_p) - c_p - B}{Z(c_p) - c_p + B} \cdot \frac{Z(c_0) - c_p + B}{Z(c_0) - c_p - B} \right] \quad (5.18)$$

where L is the membrane pore length, c_p and c_0 are solute concentration of the permeate and at the membrane surface, respectively. And parameters A, B, Z are defined as:

$$\left.\begin{aligned} A &= 2(1-2\alpha)c_p X - X^2 \\ B &= [(X - c_p)^2 + 4\alpha X c_p]^{1/2} \\ Z(c) &= (4c^2 + X^2)^{1/2} \\ \alpha &= \frac{D_1}{D_1 + D_2} \qquad \text{and} \qquad D_s = \frac{2D_1 D_2}{D_1 + D_2} \end{aligned}\right\} \quad (5.19)$$

The volume charge density (X) can be obtained using the following equation:

$$\xi = \frac{X}{c} = \frac{2q_w}{F r_p c} = \frac{16 q_0}{\left(r_p / (\kappa^{-1})\right)^2} \quad (5.20)$$

In the above equation, q_w is the membrane surface charge density, while q_0 is the dimensionless electrical potential gradient, which is defined as:

$$q_0 = \frac{1}{4} \frac{\partial \Psi}{\partial \bar{r}}\bigg|_{r=1} = -\frac{z_i F}{RT} \frac{r_p q_w}{4\varepsilon\, \varepsilon_0} \quad (5.21)$$

Eq. 5.18 provides a rigorous analytical solution relating real retention (R_r - the relationship between c_0 and c_p) and water volume flux (J_v). In more detail, Eq. 5.18 clearly shows that R_r is a function of the membrane pore radius (r_p), surface charge density (q_w), and the Debye length ($1/\kappa$), which is directly related to the solution's ionic strength. It should be noted that this equation could only be used for a 1:1 electrolyte solution. Solute was considered as a point charge and unlike the model developed in the previous chapter; this model ignores steric interaction for simplicity.

3. *Materials & Methods*

3.1 Representative membranes

Three NF membranes, denoted NF-270, NF-90 (FilmTec Corp., Minneapolis, MN), and TFC-SR2 (Koch Membrane System, San Diego, CA) were used in this study. Characteristics of these membranes have been described in detail in Chapter 3. The membrane average pore sizes have also been estimated in Chapter 4.

3.2 Trace contaminants

A natural steroid hormone –estrone, a hormone mimicking compound –bisphenol A, and two pharmaceuticals –sulfamethoxazole and ibuprofen were selected for study in this chapter. The physicochemical characteristics and origins of these compounds have been described in detail in Chapter 3. Analytical techniques for these compounds can also be found in Chapter 3.

3.3 Filtration test unit

A laboratory-scale, crossflow membrane filtration test unit – namely the Wollongong cross flow cell was used this study. A detail description of the unit is available in Chapter 3

3.4 Filtration protocol

Prior to each experiment, the membrane was stabilized at 12 bar (176.4 psi) using DI water for at least 16 hours until the permeate flux attained a constant value. The feed reservoir temperature was kept at 20±0.1°C throughout the experiment. Unless otherwise stated, permeate was recycled back to the feed reservoir.

After stabilizing the membrane (as described above), and prior to experiments with trace organic contaminants, DI water (4 L) was introduced to the feed reservoir. The cross flow and the permeate flux were adjusted to 30.4 cm/s and 15 μm/s (54 L/m^{2}h or 32.4 gfd), respectively. The natural hormone estrone was then spiked into the feed reservoir to make up a concentration of 100 ng/L. Similarly, hormone mimicking and pharmaceutically active compounds were spiked into the feed reservoir to make up a concentration of 500 μg/L. Feed and permeate samples (1 mL each) were taken for analysis at specified time intervals.

When the solution pH or ionic strength was varied, the system was equilibrated for at least one hour prior to sample collection. The solution pH was incrementally decreased from high pH to low pH whilst the solution ionic strength was incrementally increased.

4. *Role of electrostatic interactions in nanofiltration of trace organics*

4.1 Relating retention to pore radius, surface charge density, and solution chemistries

To assess the influence of the membrane characteristics (pore size and surface charge density) and solution chemistry on charge interaction, simulations were performed for 3 hypothetical NF membranes with a uniform pore size or monodisperse pores, utilising the TMS solution presented in Eqs. 5.18 to 5.21. Three different membrane pore radii of 0.34, 0.42, and 0.64 nm were selected (to represent the NF-90, NF-270, and TFC-SR2 membranes, respectively). Four different values of the surface charge density (q_w=1 x10^{-3}, 3.33 x 10^{-3}, 6.67 x 10^{-3}, and 10 x 10^{-3} (C/m^2) were assumed for each membrane. This presents a typical range of the surface charge density of both NF and RO membranes and has been used by a number of researchers for simulation and modelling purposes [129, 206]. The ionic diffusivities of a monovalent cation and anion are taken as D_1=1.956 x 10^{-9} (m^2/s) and D_2=2.033 x 10^{-9} (m^2/s). The value of other parameters were similar to that used in Wang et al. [206]: F=96487 C, ε=78.3 (C^2/Jm), ε_0=8.8542 x 10^{-12} (C^2/Jm), and T=298 K.

Salt retention as a function of the Peclet number of three hypothetical membranes described above is presented in Figure 5.2. It is noted that the membrane Peclet number is defined as $Pe = J_v \frac{L}{D_s}$, where L and D_s are the membrane pore length and diffusivity of the solute, respectively. Due to the fact that both L and D_s are intrinsic to the membrane and the solute, Figure 5.2 closely resembles Figure 4 in Chapter 4, which similarly shows retention as a function of the permeate flux for the case of steric interaction.

A profound influence of the membrane surface charge density on salt retention can be observed in Figure 5.2. Since the underlying driving force for charge repulsion depends on the membrane charge density, when it increases, so does salt retention. A similar influence of the membrane pore size can also be observed. Tighter membranes of the same surface charge density exhibit higher salt retention. It is interesting to note that such dependency of salt retention on pore size becomes less significant for membranes with high surface charge density. Likewise, the effect of surface charge density on salt retention is less profound for membranes with a small pore radius (see Figure 5.2).

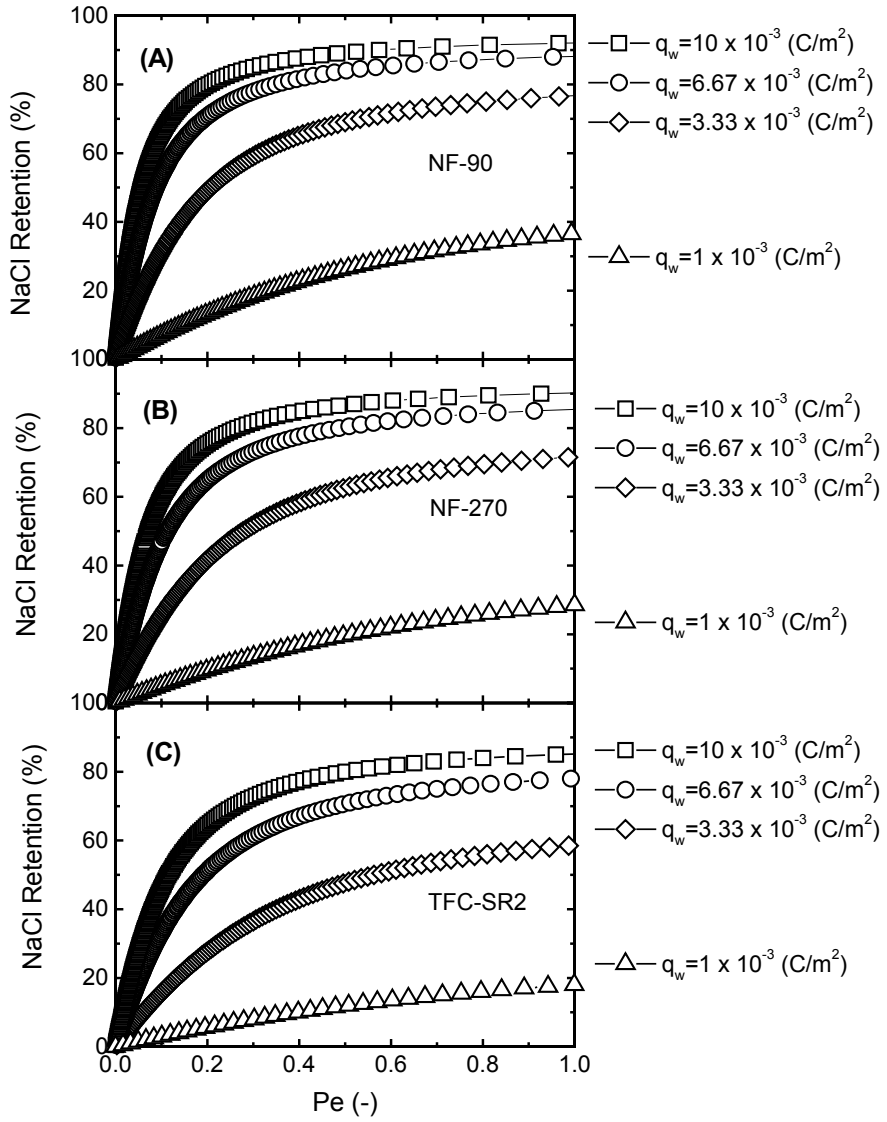


Figure 5.2: NaCl retention as a function of the membrane Peclet number Pe by 3 hypothetical NF membranes with different surface charge densities q_w. Eqs. 5.18 to 5.21 are used for the calculation. Membrane pore radii are (A) 0.34 nm, (B) 0.42 nm, and (C) 0.64 nm (equivalent to the NF-90, NF-270, and TFC-SR2 membranes, respectively). The solution ionic strength is 20 mM.

The dependency of salt retention on the solution ionic strength (or Debye length) is presented in Figure 5.3, for 4 different Peclet number values of 0.25, 0.5, 0.75, and 1.0. It appears that retention decreases as the solution ionic strength increases, following a concave curve. It is noteworthy that this model does not take into account steric interaction. Ionic solute is taken as a point charge and the Debye length can be considered as an effective radius of the solute. Consequently, for membranes of any pore size and at any Peclet number value, salt retention approaches zero as the ionic strength approaches infinity. In other words, at a sufficiently high ionic strength, charge repulsion diminishes completely and separation can only occur due to the sieving mechanism described previously in Chapter 4.

The focus of this chapter is to examine the charge interaction effect, exclusively from others. However, it is noted that a good agreement between the model and experimental data for several organic salts has been obtained by Wang *et al.* [194], when the steric effect is also taken into consideration. Nevertheless, as their model assumes that charge and steric interactions act independently, it can only be applied to NF membranes with pore radius larger than 0.5 nm. Moreover, since only a simple 1:1 electrolyte solution is considered, the model is incapable of describing complex phenomena such as negative ion retention, which may be important when examining trace organic removal and in complex background electrolyte solutions. Further investigation to model and predict retention ionic organics, particularly at trace level in a multi-electrolyte electrolyte solution, is necessary.

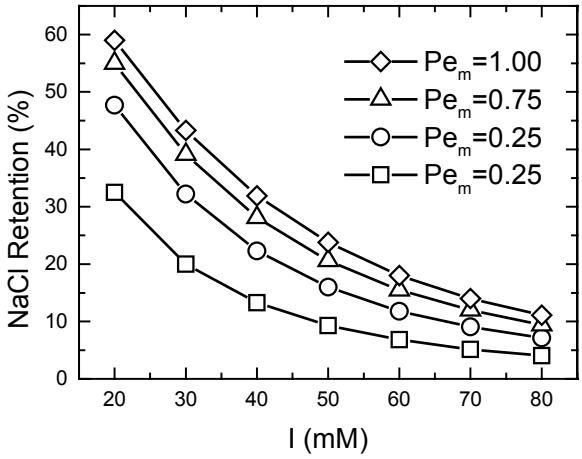


Figure 5.3: NaCl retention as a function of the solution ionic strength by a hypothetical NF membrane at different membrane Peclet number. The membrane pore radius is 0.64 nm (equivalent to the TFC-SR2 membrane) and surface charge density q_w is 3.33 x 10^{-3} (C/m^2). Eqs. 5.18 to 5.21 were used for the calculation.

As can be seen in Figure 5.2 and Figure 5.3, the model clearly illustrates the effects of the membrane properties (namely surface charge density and pore size) and solution chemistry (namely ionic strength on retention of ionic solutes). Since most (if not all) ionic organic solutes of concern are monovalent, although this model is developed for a simple 1:1 electrolyte solution, the same implications are correct for ionic organics. Such theoretical premises will be re-examined experimentally in the following sections.

4.2 Properties of nanofiltration membranes

Polymeric NF/RO membranes often contain various functional moieties such as –OH (hydroxyl), –COOH (carboxyl), and $–NH_2$ (amine). These functional groups are responsible for the formation of

fixed charge groups within the membrane polymer as it is immersed in an aqueous solution. In response to the solution pH, such function groups can protonate ($–NH_2 \rightarrow –NH_3^+$) or deprotonate ($–COOH \rightarrow –COO^-$) to give the membrane surface a positive or negative charge, respectively [133]. This charge influences the distribution of ions at the membrane-solution interface, within an electrical double layer as previously discussed. In this double layer, two regions can be observed. A layer of "fixed" ion or rather immobile ions exists immediately at the surface since they are bound to the surface by electrical forces. Further away from the surface, the ions become more mobile and this layer is called the diffusive layer. Consequently, when the ionic solution is forced to flow along a charged surface, the mobile ions will flow along a layer of more immobile ones. The electrical potential at this shear plan can be determined experimentally and is known as the ξ (zeta) potential of the membrane surface [157]. In practice, the membrane zeta potential is frequently measured and used as an indicative parameter to assess the membrane surface charge density. Techniques to measure this zeta potential have been described in detail by Childress and Elimelech [156].

Zeta potential of the three membranes NF-90, NF-270, and TFC-SR2 as a function of pH is presented in Figure 5.4. These membranes are negatively charged at high pH and they become more negative as the solution pH increases, while at low pH they become positively charged. The isoelectric point where membrane surfaces are neutral is in the pH range between 3 and 4.2 for these membranes. It can also be observed that at high pH, the NF-90 and NF-270 membranes are more negative than the TFC-SR2 membrane.

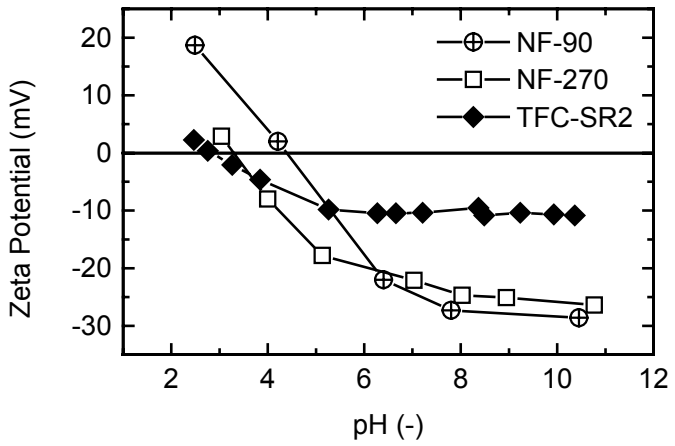


Figure 5.4: Zeta potential of NF 90, TFC-SR2, and NF 270 as a function of pH (NaCl 20 mM, $NaHCO_3$ 1 mM).

Based on the theoretical analysis above, one could expect that the membrane zeta potential influences retention of ionic solutes in the same way as surface charge density since they are

directly related to each other. This is clearly illustrated in Figure 5.5. There is a decline in salt retention by the NF-90 and NF-270 as the solution pH decreases. This effect is less significant for the TFC-SR2 possibly because it is less negatively charged. Salt retention is also in good agreement with the membrane pore size. The NF-90 exhibits highest retention while the most open pore size TFC-SR2 membrane shows the lowest retention. Minimum salt retention can also be observed for the NF-270 and TFC-SR2 membranes near the membrane isoelectric point, where the membrane surface is neutral and separation is solely due to the sieving mechanism. This phenomenon is however not observed for the NF-90 membrane, possibly due to its small pore size.

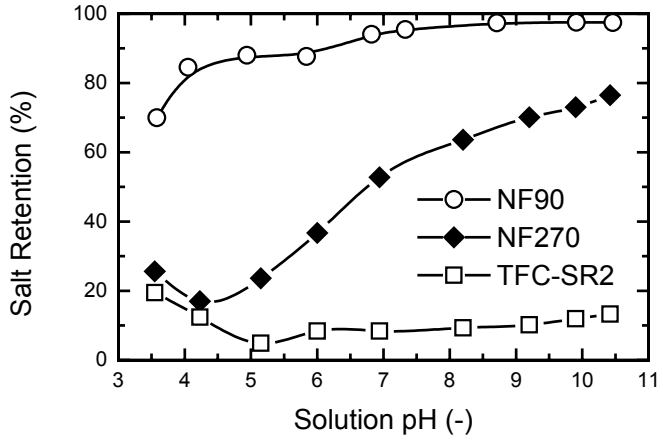


Figure 5.5: Salt retention (measured by conductivity) by three membranes NF 90, NF 270, and TFC-SR2 as a function of pH (NaCl 20 mM, $NaHCO_3$ 1 mM).

Physicochemical properties of inorganic ions such as Na^+ and Cl^- are relatively independent of the solution pH. In other words, these ions always carry a constant fixed charge at any pH. Therefore, phenomena observed in Figure 5.5 are solely due to the membrane surface charge density. As physicochemical properties of organics may depend strongly on the solution pH and other solution chemistries, a much more complex behaviour is expected for trace organics.

4.3 Speciation and physicochemical properties of trace organics

Certain elements or compounds may exist in aqueous solution in various forms (species) and the distribution of these species (or the speciation process) often strongly depends on the specific solution conditions of pH, temperature, pressure, ionic strength, and to some extent the presence of other entities in the solution [209]. Understanding the speciation process is highly critical as various species may behaviour quite differently in NF/RO filtration processes due to a range of factors including size and charge, amongst other more complex physicochemical properties of the particular species. Although the effects of chemical speciation of numerous inorganics have been exquisitely discussed by David [209] understanding with regards to trace organic speciation

influence on retention is still limited. Species distribution can be influenced by various mechanisms such as acid-base transformation, complexation, precipitation, and oxidation-reduction. Amongst these, acid-base transformation is probably the most important mechanism for NF/RO membrane filtration involved trace organic contaminants.

In a typical membrane filtration process where temperature, pressure and ionic strength vary in a moderate range, speciation depends mostly on the solution pH. Functional moieties of many trace organics are readily dissociable in accordance with the solution pH. Those contain carboxyl or hydroxyl functional groups can deprotonate to gain a negative charge, while those with amine functional group can protonate to gain a positive charge. Such speciation processes depend on the compound dissociation constant or the pK_a value as they are demonstrated in Figure 5.6 trace organics selected for study here except carbamazepine, which has a relatively low pK_a value of 2.3 (see Chapter 3).

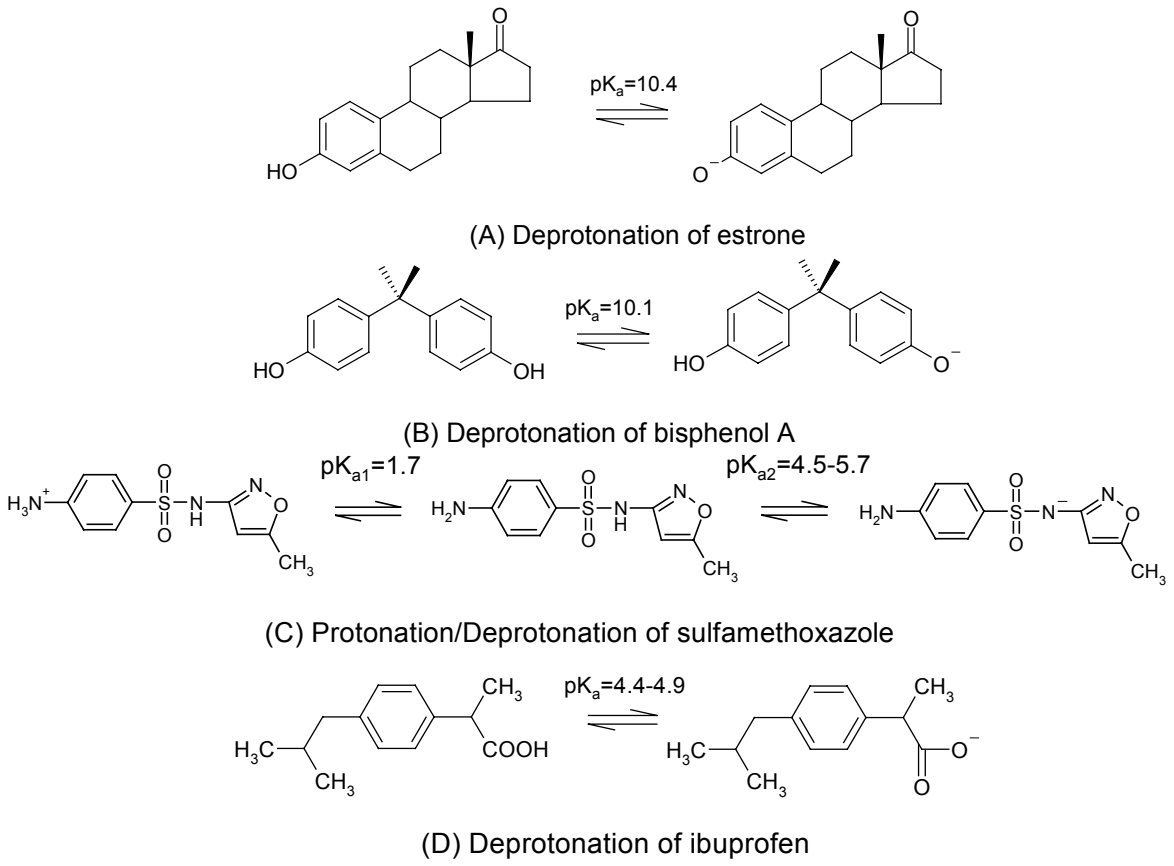


Figure 5.6: Protonation and/or deprotonation of (A) estrone, (B) bisphenol A, (C) sulfamethoxazole, and (D) ibuprofen.

The speciation of estrone, bisphenol A, sulfamethoxazole, and ibuprofen is presented in Figure 5.7. The figure clearly depicts the effects of speciation on the charge of the corresponding trace organics, although other important physicochemical properties, particularly size, hydrophobicity, solubility, and diffusivity can also be strongly influenced by speciation. Solubility-pH [210] and hydrophobicity-pH [167] profiles of ibuprofen have been experimentally examined and they appear to closely resemble the speciation of this compound as shown in Figure 5.7. As discussed in other parts of this thesis, it is noteworthy that these properties can also govern the behaviour of trace organic solutes in NF/RO filtration processes. Nevertheless, the focus of this chapter is on charge interaction and the impacts of such physicochemical properties on retention will only be discussed when they are essential.

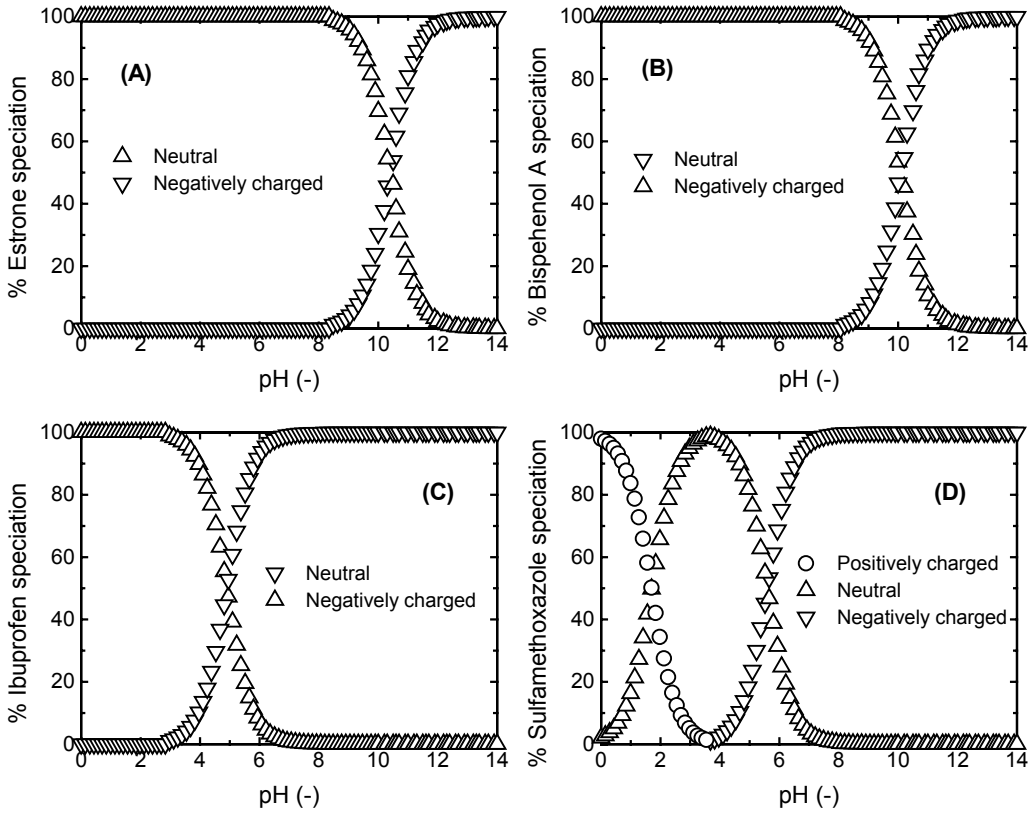


Figure 5.7: Speciation of (A) ─ estrone (pK_a = 10.4), (B) ─ bisphenol A (pK_a = 10.1), (C) ─ ibuprofen (pK_a = 4.9), and (D) ─ sulfamethoxazole (pK_{a1} = 1.7 and pK_{a2} = 5.6-5.7).

4.4 Nanofiltration of charged organic contaminants

Ibuprofen is an acidic pharmaceutical. Given that its pK_a value is approximately 4.9, the compound is negatively charged at high pH (see Figure 5.7). Similarly, due to the deprotonation of the diamine group, sulfamethoxazole can also become negatively charged at pH higher than the pK_a value of this amine functional group, which is again in the range of 5.6-5.7. To examine the hypothesis that

charge repulsion can enhance retention, a set of experiments has been conducted for these two pharmaceutically active compounds (PhACs) at pH 8.0 where they exist predominantly in an anionic form (Figure 5.7). Concentration of sulfamethoxazole and ibuprofen in the feed and permeate as a function of time following filtration by the NF-270, NF-90, and TFC-SR2 membranes is shown in Figure 5.8 and Figure 5.9, respectively.

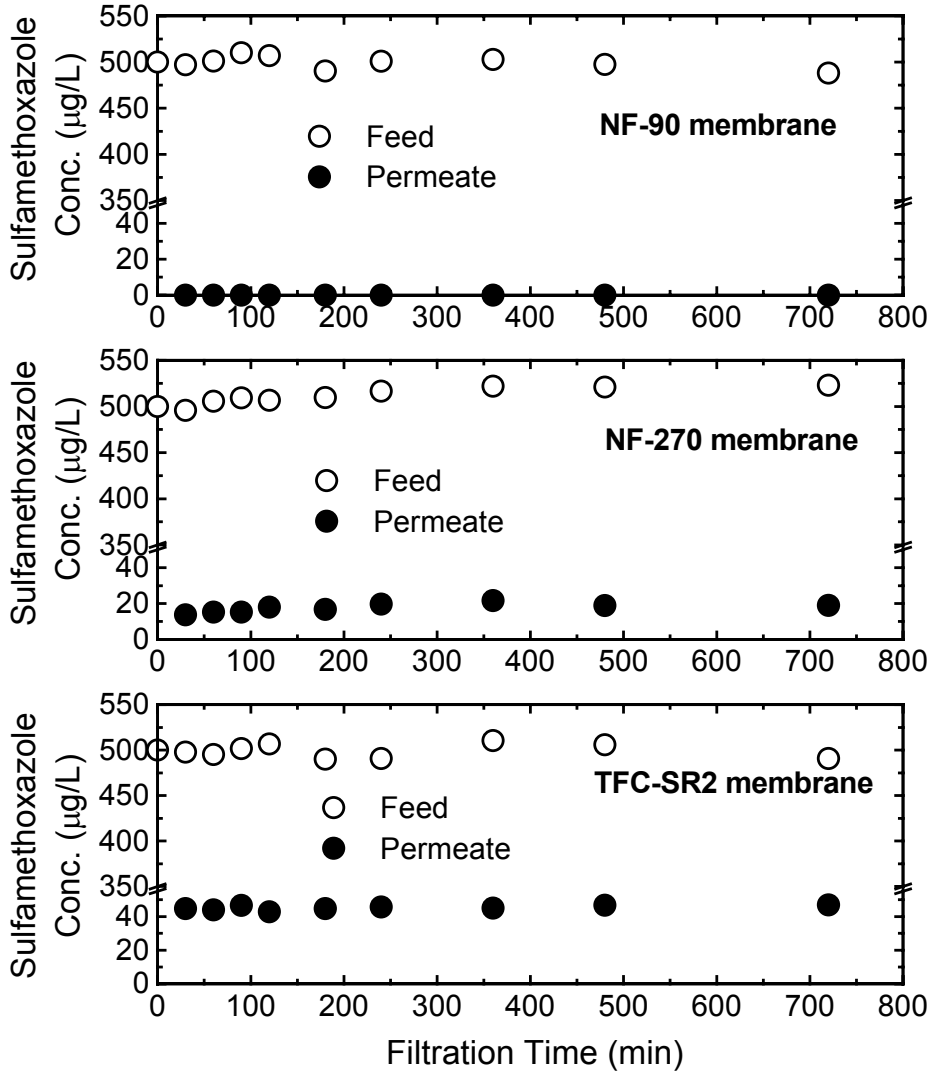


Figure 5.8: Permeate and feed concentrations of sulfamethoxazole as a function of filtration time for the NF-90 membrane (top), NF-270 membrane (middle), and TFC-SR2 membrane (bottom). The feed solution contained 500 μg/L sulfamethoxazole in a background electrolyte solution containing 20 mM NaCl and 1 mM $NaHCO_3$. Other experimental conditions were as follows: cross flow velocity = 30.4 cm/s, permeate flux = 15 μm/s, pH ≈ 8.0, and temperature = 20.0°C.

In contrast to neutral steroid hormones and hormone mimicking compounds, these two PhACs did not adsorb to the membrane and the feed concentration remained constant throughout the experiments. This is because of charge repulsion with the membrane surface. At pH 4.0 or higher,

the membrane is also negatively charged as can be seen from the zeta potential graph presented in Chapter 3. It is noteworthy that at pH lower than its pK_a value, ibuprofen can adsorb significantly to the membrane polymer, due mostly to its relatively high log K_{ow} value.

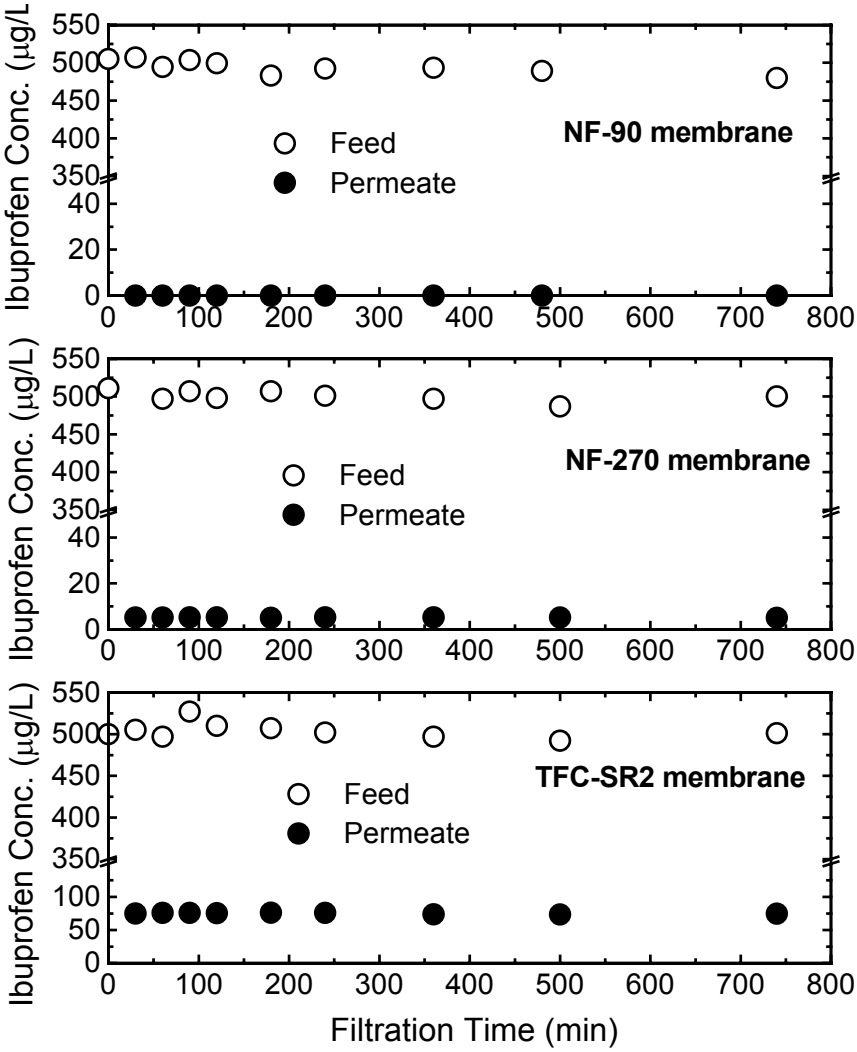


Figure 5.9: Permeate and feed concentrations of ibuprofen as a function of filtration time for the NF-90 membrane (top), NF-270 membrane, and TFC-SR2 membrane (bottom). The feed solution contained 500 μg/L ibuprofen in a background electrolyte solution containing 20 mM NaCl and 1 mM $NaHCO_3$. Other experimental conditions were as follows: cross flow velocity = 30.4 cm/s, permeate flux = 15 μm/s, pH ≈ 8.0, and temperature = 20.0 ^oC.

Additional experiments were conducted to investigate the charge repulsion effects of negatively charged hormones and hormone mimicking compounds, which can adsorb to the membrane when they are neutral. A similar phenomenon can be observed for the steroid hormone estrone and hormone mimicking compound bis-phenol A when they are in anionic form (solution pH of 11.5 and 11, respectively). As can be seen from Figure 5.10 and Figure 5.11, no adsorption of estrone or bis-phenol A can be observed at such pH. Retention of anionic estrone was approximately 30%

higher than that of the neutral species, while retention of anionic bis-phenol A was enhanced by almost 50% as compared to its neutral form (see Chapter 4). This is predominantly attributed to charge repulsion between the negative membrane surface and negatively charged estrone and bis-phenol A. It is noteworthy that to some limited extent, this is also attributed to the fact in an anionic form, these solutes do not partition into the membrane and sorption diffusion transport of such solutes through the membrane polymer does not occur. Further discussion about the sorption diffusion transport of trace organics in NF/RO membranes can be found in Chapter 7.

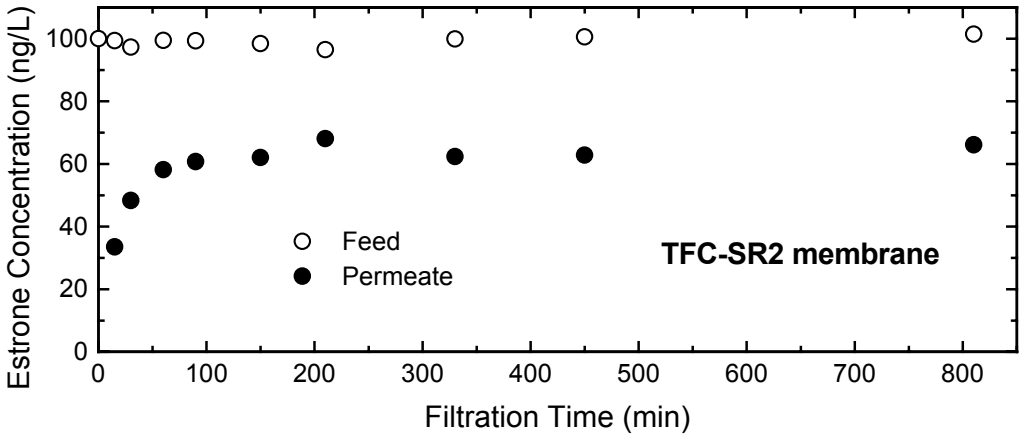


Figure 5.10: Permeate and feed concentrations of estrone as a function of filtration time for the TFC-SR2 membrane. The feed solution contained 100 ng/L estrone in a background electrolyte solution containing 20 mM NaCl and 1 mM $NaHCO_3$. Other experimental conditions were as follows: cross flow velocity = 30.4 cm/s, permeate flux = 15 μm/s, pH ≈ 8.0, and temperature = 20.0°C.

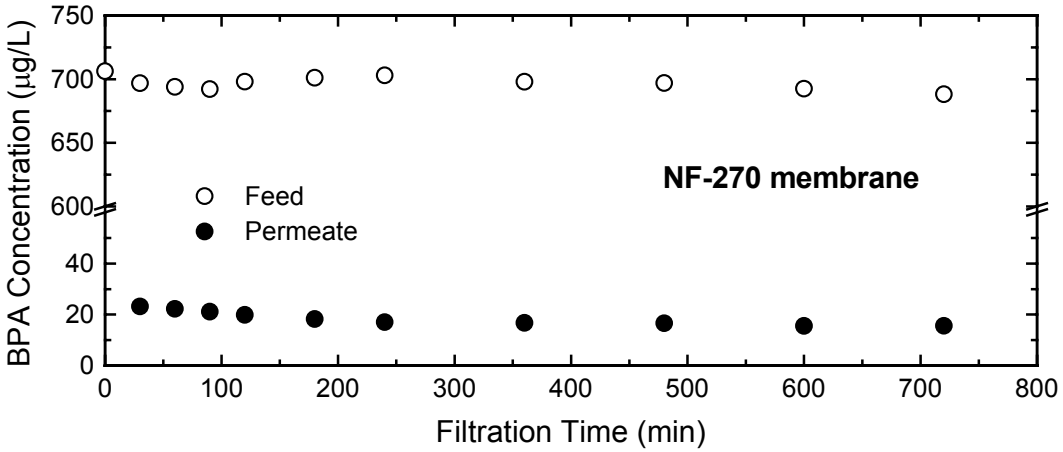


Figure 5.11: Permeate and feed concentrations of bis-phenol A as a function of filtration time for the NF-270 membrane. The feed solution contained 700 μg/L bis-phenol A in a background electrolyte solution containing 20 mM NaCl and 1 mM $NaHCO_3$. Other experimental conditions were as follows: cross flow velocity = 30.4 cm/s, permeate flux = 15 μm/s, pH ≈ 8.0, and temperature = 20.0°C.

Results obtained from the pharmaceutically active compound selected in this study also clearly indicate that charge repulsion between solute and the membrane surface has enhanced the separation process (Figure 5.12). At pH 8, the NF-90 membrane completely rejects both sulfamethoxazole and ibuprofen. No sulfamethoxazole and ibuprofen can be detected in the permeate. Retention by the NF-270 for both compounds is also high, 99 and 96 % for ibuprofen and sulfamethoxazole, respectively. It is interesting to note that although ibuprofen has a relatively smaller molecular weight (206 g/mol) than that of sulfamethoxazole (253 g/mol), its retention value by the NF-270 is in fact higher. One can hypothesize that since ibuprofen is an acidic compound, it may dissociate stronger than sulfamethoxazole and hence results in stronger charge repulsion interactions. Retention due to charge interaction is most apparent with the very loose nanofiltration membrane TFC-SR2. Retention of both ibuprofen and sulfamethoxazole is considerably higher than predicted by steric interaction mechanism presented in Chapter 4.

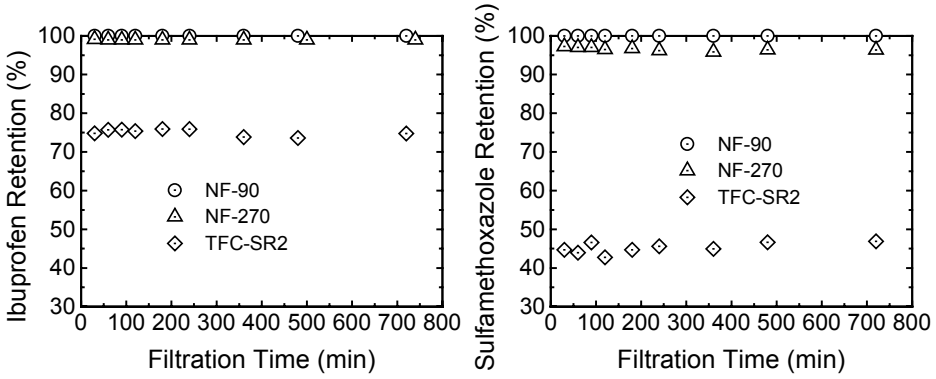


Figure 5.12: Retention of (a) ibuprofen and (b) sulfamethoxazole by the NF-270, NF-90, and TFC-SR2 membranes as a function of time. The feed solution contained approximately 500 μg/L of the corresponding pharmaceutically active compound in a background electrolyte solution containing 20 mM NaCl and 1 mM $NaHCO_3$. Other experimental conditions were as follows: cross flow velocity = 30.4 cm/s, permeate flux = 15 μm/s, pH ≈ 8.0, and temperature = 20.0°C.

Results reported here indicate that loose nanofiltration membranes can be used effectively to remove ionisable trace organics. This has an important implications for in practice as most ionic trace organics do not absorb to activated sludge and can be persistent to the biological treatment process of conventional wastewater treatment plants, hence more likely to present in secondary treated effluent than some of their hydrophobic counterparts.

4.5 Effect of pH on the retention of pharmaceuticals

The solution pH can have a dramatic effect on the membrane surface charge (see Figure 5.4). As mechanistically demonstrated in section 4.1, this in turn will have a significant influence on charge interaction between the membrane surface and charged solutes, and hence the contribution of

charge repulsion toward the separation of charged solutes. As can be seen in Figure 5.7, speciation of certain trace organics can also be strongly dependent on solution pH. In other words, some trace organics can vary their form from a neutral to positively charged or negatively charged species in accordance to the solution pH and their pK_a value. In parallel to the former phenomenon, this can also influence charge interaction between the membrane surface and charged solutes. Consequently, the solution pH can be a critical factor governing electrostatic interaction in a nanofiltration membrane filtration system involving ionisable trace organics.

Retention of sulfamethoxazole by three membranes with different pore size is presented in Figure 5.13. The NF-90 membrane is a tight nanofiltration membrane with an average pore radius of 0.34 nm, which is smaller than molecular size of these two pharmaceuticals. The equivalent Stokes radii of ibuprofen and sulfamethoxazole are 0.34 and 0.38 nm, respectively (calculated using the Wilke and Chang and the Stockes-Eistein equations [211]). The effect of solution pH on retention is therefore almost indiscernible for this membrane. At pH less than 6, sulfamethoxazole retention by the NF-90 membrane is 98% while at pH higher than 6, complete sulfamethoxazole retention of 100% can be achieved with this membrane.

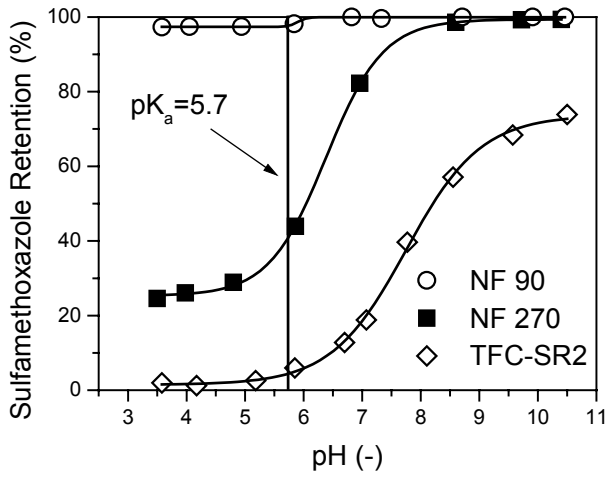


Figure 5.13: Sulfamethoxazole retention by the NF-90, NF-270, and TFC-SR2 membranes as a function of pH. The feed solution contained approximately 500 μg/L of sulfamethoxazole in a background electrolyte solution containing 20 mM NaCl and 1 mM $NaHCO_3$. Other experimental conditions were as follows: cross flow velocity = 30.4 cm/s, permeate flux = 15 μm/s, and temperature = 20.0°C.

In contrast, there is a marked effect of pH on sulfamethoxazole retention by the loose NF-270 and very loose TFC-SR2 nanofiltration membranes. Retention rises from only 25 % to as high as 100 % for the NF-270 membrane as the solution pH increase from 3.5 to 10.5 (Figure 5.13). Similarly, a

remarkable increase of almost 70% (Figure 5.13) in retention can also observed with the very loose TFC-SR2 nanofiltration membrane. In this example, it is evident that electrostatic repulsion is the dominant removal mechanism for these two membranes. Steric interaction contributes to the separation of sulfamethoxazole by the NF-270 membrane to a small degree whereas it is probably absent in the case of the very loose TFC-SR2 membrane. This is mostly attributed to the compound's high dipole moment and its cylindrical shape as discussed previously in Chapter 4.

It is interesting to note that sulfamethoxazole retention responds to the solution pH in a sigmoidal pattern, resembling that of the compound speciation curve. However, the inflection point appears to deviate from the second pK_a value of sulfamethoxazole (in the range of 5.6 to 5.7). A similar observation can also be inferred from the data reported by Bellona and Drewes [132]. This can partly be attributed to the negative proton retention effect often observed in an acidic condition [133, 212]. The phenomenon was first observed by Childress and Elimelech [133], who reported a significant passage of protons through nanofiltration membranes in acidic conditions. This is because H^+ is more mobile or permeable than other cations (i.e. Na^+) in the solution due to its relatively small hydrated size. When the ratio of the more permeable ion to the less permeable ion is low, negative retention of the more permeable ion is possible [213]. Negative retention of protons of up to 400% has been reported for the loose NF-45 membrane at pH 4.5 [212]. Due to the passage of protons through the membrane pore, pH at the membrane pore and boundary layer would be lower than that at the bulk solution, which to some extent explains the deviation between the inflection point and the pK_a value of sulfamethoxazole as seen in Figure 5.13.

It is also appears that such negative proton retention phenomenon is more severe for loose nanofiltration membranes where Donnan exclusion plays a more significant role [212]. This is consistent with the fact that deviation from the pK_a value is most profound for the very loose TFC-SR2 membrane followed by the loose NF-270 membrane and it is almost negligible for the tight NF-90 nanofiltration membrane. It is noteworthy that variation of the membrane charge surface as a function of pH can further complicate the phenomenon. Negative proton retention by the NF-270 and TFC-SR2 were confirmed by measuring pH of the feed and permeate samples. However, the difference was relatively small, in the range of 0.2 – 0.3 pH unit at pH 4. Although it is possible that due to the small pore volume, pH at the membrane pore and boundary layer can be significantly less than that of the bulk solution, other factors may also contribute to this deviation seen in Figure 5.13.

Retention of ibuprofen as a function of the solution pH was also investigated and the results are presented in Figure 5.14. As the solution pH decreases, ibuprofen retention by the TFC-SR2 membrane decreases due to the subsidence of electrostatic interaction as discussed above. Below pH 5, ibuprofen retention appears to increase as pH decreases. This is however attributed to the adsorption of ibuprofen to the membrane when the compound is neutral due to its relatively high hydrophobicity or log K_{ow}. A marginal decrease in retention by the NF-270 membrane can be observed while the NF-90 membrane exhibits 100% retention throughout the investigated pH range as the average pore size of these two membranes is significantly smaller than that of the TFC-SR2.

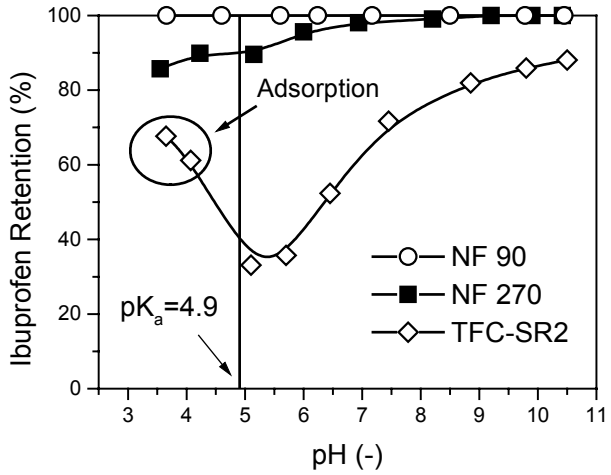


Figure 5.14: Ibuprofen retention by the NF 90, NF 270, and TFC-SR2 membranes as a function of pH. The feed solution contained approximately 500 μg/L of sulfamethoxazole in a background electrolyte solution containing 20 mM NaCl and 1 mM $NaHCO_3$. Other experimental conditions were as follows: cross flow velocity = 30.4 cm/s, permeate flux = 15 μm/s, and temperature = 20.0°C.

4.6 Effect of ionic strength on the retention of pharmaceuticals

Since the solution ionic strength is directly related to the Debye length or the double layer thickness at the membrane surface, which in turn governs electrostatic interaction in an NF/RO membrane filtration system, it is expected to exhibit some influence on the separation process of charged solutes. Indeed, experimental data presented in Figure 5.15 appear to strongly support such a premise. When comparing Figure 5.3 to Figure 5.15, it can be observed that the model developed in section 2 has qualitatively depicted the phenomenon very well. As ionic strength increases, the solution Debye length is shortened. In other words, electrostatic interaction is screened and hence results in a lesser extent of electrostatic interaction. The influence of ionic strength on retention is absent when sulfamethoxazole exists predominantly in a neutral form. This again consistently

confirms that the effect of ionic strength on retention of negatively charged sulfamethoxazole is induced by the suppression of electrostatic interaction.

Results reported here also highlight the importance of charge repulsion as a removal mechanism of charged solution in NF membrane filtration processes. At low ionic strength, a remarkable retention can be achieved with negatively charged sulfamethoxazole while retention of its neutral species appears negligible (see Figure 5.15). Fortunately, for most water recycling applications, ionic strength or salinity of the secondary treated effluent is relatively low. This may open a scope for the use of loose NF membranes to remove ionisable trace organics, which may be persistent to the biological treatment process and therefore exist in secondary effluents.

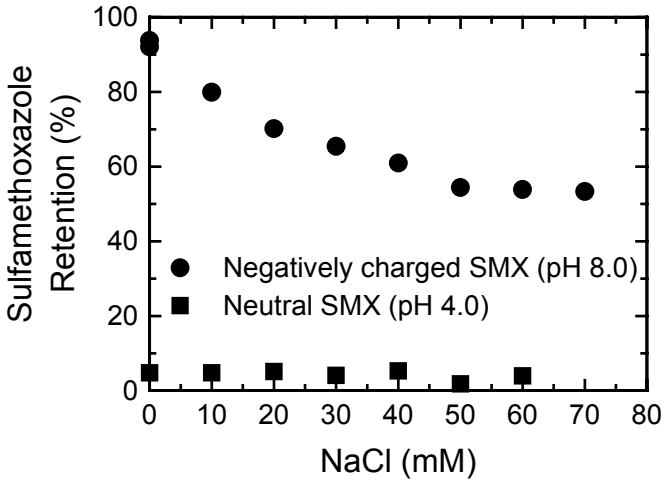


Figure 5.15: Sulfamethoxazole retention by the TFC-SR2 membrane as a function ionic strength at pH 8.0 and 4.0. The feed solution contained approximately 500 μg/L of sulfamethoxazole in a background electrolyte solution containing 20 mM NaCl and 1 mM $NaHCO_3$. Other experimental conditions were as follows: cross flow velocity = 30.4 cm/s, permeate flux = 15 μm/s, and temperature = 20.0°C.

5. *Conclusions*

In this chapter, the role of charge interaction in the separation of ionisable trace organics using NF membranes was explored. Although limited to an ideal 1:1 electrolyte solution and the assumption that charge solute is considered as a point charge, the TMS model could be used to extensively and theoretically examine various solution chemistry and membrane properties effects on retention of anionic trace organics. Such findings were consistently supported by experimental data obtained with a steroid hormone, a hormone-mimicking compound, and two pharmaceuticals in their anionic forms.

Retention behaviour of charged organics is quite similar to that of inorganic salts. Simulated results obtained from the TMS model are in good agreement with data from the nanofiltration experiments of trace organics. The membrane charge density (represented by the membrane zeta potential) and average pore size are two critical parameters governing the separation process of charged trace organics. It was also confirmed that an increase in the solution ionic strength would suppress the Debye length, and hence, reduce the extent of charge repulsion.

Results reported in this chapter indicate that the ionic organic solutes do not adsorb to the membrane polymer, due primarily to electrostatic repulsion. Negatively charged trace organics exhibit high retention, even with the very loose TFC-SR2 membrane. It appears that the solute pH can have a dramatic effect on retention as it influences both the speciation of ionisable trace organics and the membrane surface charge density. The pH effect was most obvious for loose nanofiltration membranes when charge repulsion was the dominating retention mechanism. Retention was found to be correlated to pH following a sigmoidal shape in the case of sulfamethoxazole.

Chapter 6

Adsorption

1. *Introduction*

Reverse osmosis and nanofiltration membranes were initially designed for desalting and softening purposes, where salts are primary solutes of concern. In these cases, solute-membrane interactions were mostly explained by electrostatic interactions. While sorption of cationic and anionic ions to and subsequent diffusion through the membranes via ion exchange processes are a basic foundation of the sorption-diffusion transport mechanism in both NF and RO membranes, adsorption of organic solutes to the membranes is often neglected in many textbooks [214].

Water is a universal solvent of life. A vast number of constituents can be dissolved in it, many are organics and quite adsorptive. Adsorption is therefore, inherent in any NF/RO membrane filtration processes. However, adsorption is commonly associated with fouling. Mulder has stated "(it) already occurs before pressure has been applied and the membrane process has been started" [215]. As soon as the membrane is in contact with the solution, organic molecules will adsorb at the membrane surface due to various physicochemical interactions, e.g., hydrophobic interaction (dispersive forces), electrostatic attraction, or weak chemical reactions such as hydrogen bonding.

The nature of the adsorption process has been the focus for many studies to alleviate membrane fouling. Most of these studies place emphasis on macro organics such as bovine serum albumin (BSA) or surrogate organic matter such as NOM, humic acids, and fulvic acids, see for example [16, 140, 216-218]. It is only recently that concern over trace organic contaminants, particularly during water recycling, has prompted a new aspect about this issue. However, adsorption of trace organic contaminants to NF/RO membranes is not new. Chian *et al.,* [8] reported it almost three decades ago. However, to date, there has been a dearth of information about this important phenomenon in NF/RO filtration processes.

Adsorption of trace organics to polymeric membranes has an important implication on how they can be used and designed for the future application. It is indeed essential in drug control and release, where adsorption and subsequent release of drugs in a polymer encapsulated pill provides a constant flux of medicine to the patients over time [219]. In NF/RO membrane filtration applications, although undesirable, there is a possibility that adsorption of trace organics to the membranes can assist the removal process so long as these contaminants do not reach the permeate and their leaching during membrane cleaning can be properly managed.

This chapter investigates the adsorptive behaviour of steroid hormones and hormone mimicking compounds to NF/RO membranes in an attempt to elucidate fundamental understanding about the adsorption process and to establish a relationship between the membrane and trace contaminant properties. Interaction between the membrane polymeric matrix and trace contaminants under various solution chemistries will be cortically examined. Several risk implications associated with trace contaminant adsorption will also be evaluated.

2. *Adsorption in membrane filtration processes*

2.1 The nature of adsorption

In an NF/RO membrane filtration process, adsorption is governed by interactions between the membrane and solute, solute and water, and solute and solute. In this case, the membrane, solute, and water are adsorbent, adsorbate, and solvent, respectively. In general, the solute-water and (to a limited extent) solute-solute interactions are less significant than the membrane-solute interaction. For this reason, most available studies, to date, focus on membrane-solute interaction.

Adsorption can be physical or chemical in nature or both. Physical adsorption arises from dispersive and electrostatic interaction and chemical adsorption is a result of chemical bonding. The former is a completely reversible process, while the later can be irreversible for strong chemical bonds such as polymerisation or reversible for weak secondary chemical bonds such as hydrogen bonding and complexation. The boundary between physical and chemical interactions is however quite blurred. Very often adsorption involves both and the term “physicochemical” is commonly used without any attempt to separate the two to describe physical and chemical properties of both the membrane polymers and organic solutes.

2.1.1 Physical interactions

Omitting the interaction between electric field, for physical adsorption, the membrane-solute energy potential can be expressed as [220]:

$$\phi = \phi_D + \phi_R + \phi_{F\mu} \tag{6.1}$$

Φ_D is dispersion energy. This is also commonly known as hydrophobic interaction where two hydrophobic surfaces avoid water and attach to each other to achieve a lower potential energy. Φ_R is close range repulsion energy. And $\Phi_{F\mu}$ is interaction energy between permanent dipoles. The first two terms (Φ_D and Φ_R) are non-specific and are operative in all adsorbate-adsorbent systems. They are given as:

$$\phi_D = -\frac{A}{r^6} \tag{6.2}$$

$$\phi_R = +\frac{B}{r^{12}} \tag{6.3}$$

Where A and B are constants, r is the distance between adsorbate and adsorbent, and the minus sign in Eq. (6.2) indicates attraction. Ignoring the dipole-dipole interaction, the dispersive and repulsive interactions form the Lennard-Jones potential, with an equilibrium at which $\Phi_D+\Phi_R$ is minimum (at a distance r_0, see Figure 6.1). The energy potential arises from these two terms as a function of r is shown in Figure 6.1. Lennard-Jones theory is widely used in gas adsorption; however, its physical nature is universally correct and can also be applied to a membrane-trace organic system.

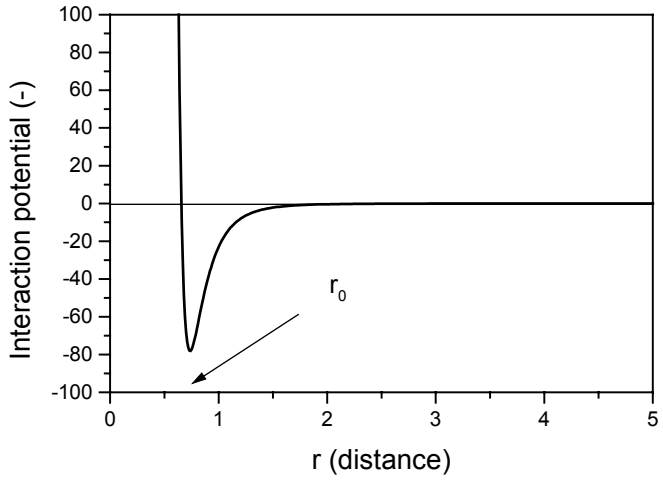


Figure 6.1: The energy of interaction between adsorbate and adsorbent as a function of their distance.

Positive potential indicates an unfavourable condition for adsorption. Stable conditions can be achieved at r_0, where the energy potential is minimum. As can be seen in Figure 6.1, Lennard-Jones theory clearly illustrates the reversibility nature of physical adsorption.

The dipole-dipole interaction arises from charges and is only operative where permanent dipoles exist. Dipole-dipole interaction is site-specific and the angle between dipole axes is an important factor affecting its energy. It contributes to the physical interaction potential to a lesser extent as compared to dispersion and repulsive interactions. However, dipole-dipole interaction may play an important role in orientating solute-membrane functional group interactions, which are essential in other site-specific adsorption mechanisms.

2.1.2 Chemical adsorption

Chemical adsorption can arise via weak secondary bonds such as hydrogen bonding and complexation or strong permanent reactions e.g., polymerisation. However, there is no evidence suggesting that polymerisation between organic solutes and the membrane can occur under typical filtration conditions. Although irreversible adsorption of organics, which results in irreversible fouling is often mentioned in membrane literature, this should be understood in practical sense, where irreversible fouling (or adsorption) is defined as fouling that cannot be removed by common membrane cleaning techniques. Adsorption due to chemical interaction in a membrane filtration process is therefore reversible. In general, adsorption energy is below 15-20 kcal/mol, that is desorption can be easily achieved with mild condition alteration such as changing temperature or pressure.

Complexation is a common interaction between organics and heavy metals. In a membrane filtration system, it is expected that hydrogen bonding is more prominent as both adsorbate and adsorbent are organic. Trace organic contaminants typically have functional groups; some of them such as carbonyl and hydroxyl groups can strongly participate in the formation of hydrogen bonding with the membrane functional groups as a proton donor or acceptor. Hydrogen bonding has been proven to be the primary adsorption mechanism between steroid hormones such as progesterone and their receptors [221]. Hydrogen bonding is also essential in forming the double helix coil in a DNA strand. It is well known that conformation of such DNA (or the formation and rupture of such hydrogen bonds between amino acids) can be easily manipulated by a small variation in temperature. However, clear evidence supporting hydrogen bonding formation between trace organics and the membrane functional groups have yet to be reported. Trace organics often possess

both hydrogen bonding capacity and high hydrophobicity at the same time. It is therefore, possible that both chemical (hydrogen bonding) and physical (hydrophobic interactions) adsorptions occur simultaneously in a membrane filtration system involving trace organics.

2.2 Sorption diffusion – a transport mechanism

Transport mechanisms in nanofiltration and reverse osmosis membranes have not yet been well characterised. Several models exist and are being used concurrently to explain the transport phenomena. Three most prominent ones are the pore flow model [122, 192, 193, 222], sorption capillary model of Sourirajan [116], and sorption diffusion model [186, 187, 222].

In the pore flow model, solutes and water (solvent) are separated by pressure-driven convective flow through tiny pores. Solutes are excluded (filtered) as steric hindrance prohibits their permeation through the membrane pores (see Chapter 4). This model is more intuitive than others as it is closer to normal physical phenomena. However, it can only be applied to NF membranes with real pores. In the sorption diffusion model, both water (solvent) and solutes can dissolve in the membrane polymeric material and then diffuse through the membrane due to a chemical concentration gradient. In other words, this model relies on the fact that reversible adsorption and desorption of solutes to (and from) the membrane occurs simultaneously and chemical concentration gradient induced by pressure is the driving force. This model can be applied to both NF and RO membranes. The choice between the pore flow model and sorption diffusion model also depends on the solute physicochemical properties. The sorption capillary model can be seen as a hybrid between the pore flow and sorption diffusion model. It was developed and used by Sourirajan and coworkers to explain various transport phenomena of micro organics in NF and RO membranes [116], including the negative rejection of some phenolic compounds. The sorption diffusion transport of some trace organics in NF/RO membrane filtration processes is described in detail in Chapter 7.

Amongst these three models, the sorption diffusion model is the most widely accepted. Not surprisingly, adsorption and desorption of trace organic contaminants play an essential role in NF/RO membrane filtration processes.

2.3 Adsorption mechanisms

2.3.1 Hydrophobic interactions

Hydrophobic interactions are inherent in membrane filtration of water and wastewater involving hydrophobic organic contaminants. Proteins, which are quite hydrophobic, tend to strongly bind to hydrophobic materials. There is a clear trend to develop membranes based on hydrophilic rather than hydrophobic polymers to minimise membrane fouling. However, hydrophilic polymers are less stable and are often prone to hydrolysis. It is therefore a typical practice to chemically modify the membrane surface to make it more hydrophilic or blend hydrophobic and hydrophilic materials together.

Adsorption of hydrophobic organics to NF/RO membranes has been reported in various studies [9, 69, 134, 205, 214, 223] (see also Chapter 4). Kiso *et al.,* [69, 134, 205] reported a characteristic correlation between the partitioning coefficient of adsorptive organic solutes to the membranes - log K (or adsorption) and the hydrophobicity of numerous pesticides and phthalates. Their results clearly demonstrate a central role of hydrophobic interactions in adsorption. However, the issue appears to be more complicated because in order to get a linear correlation, they have to arbitrarily divide the compounds under study into two groups (see Figure 6.2). A similar finding was also reported by Van der Bruggen *et al.,* [214] when they investigated flux decline due adsorption of organics to NF membranes. Molecular weight of the organics used in their study ranges from 32 to 342 g/mol. Concentration of each organic component was 10 mmol/L and each organic was separately studied. Interestingly, several compounds with negative log K_{ow} were also found adsorbed to the membranes. Adsorption was strongly correlated to flux decline, which according to the authors was attributed to pore blocking [214].

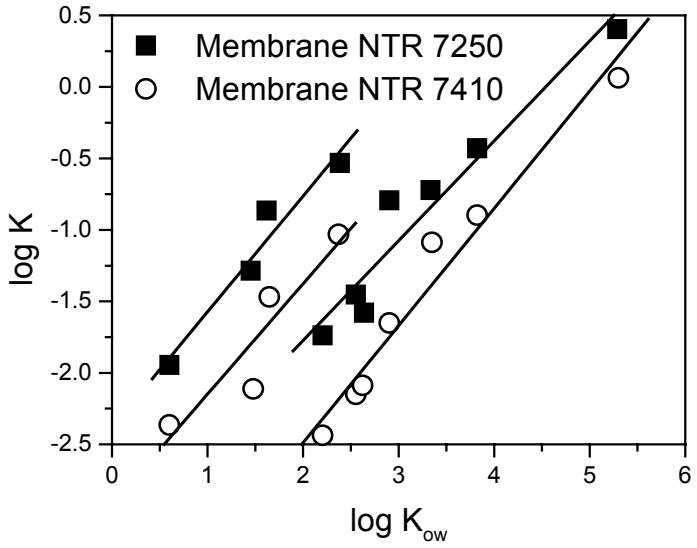


Figure 6.2: The partition coefficient (log K) of various pesticides between the membrane and bulk solution as a function of their log K_{ow} (data from [134]).

Hydrophobic interactions are non-specific. Adsorption depends strongly on the hydrophobic surface available on the membrane surface and consequently the membrane surface roughness. If the membrane pore size is large enough, adsorption can also happen inside the pore. However, the membrane polymer matrix can be quite flexible and the conformation of the polymer chains within the membrane can change constantly subject to the hydrodynamic conditions. In this case, available hydrophobic surface may be of little relevance to the adsorption (or partitioning) process in comparison to the presence of hydrophobic polymer chains within the membrane. The picture remains blurred and there are no doubts that further dedicated research is imperative to fully understand the actual role of hydrophobic interactions in adsorption.

2.3.2 Hydrogen bonding

The nature of hydrogen bonding and hydrophobic interactions is distinctively different. The former relies on an electron pair shared between the functional groups of the adsorbate (trace organics) and the membrane polymer, or in other words, the hydrophilic domain within the membrane. The latter relies on the water exclusion nature between two hydrophobic surfaces. However, hydrophilic and hydrophobic domains coexist in any polymeric membrane and hence both adsorption mechanisms may coexist and may be difficult to distinguish.

Hydrogen bonding plays a vital role in shaping the properties of water. It is indeed intra hydrogen bonding between water molecules that maintains water in a liquid form under a normal atmospheric

conditions. When considering the sorption diffusion transport model, water is thought to adsorb to the membrane via hydrogen bonding [116]. Since this is a type of specific adsorption, competition for an adsorptive site between water and organics that are capable of forming a hydrogen bond with the membrane polymer will result in flux decline if the concentration of such organics is sufficiently high. As adsorptive sites are limited, this can occur even with a small amount of adsorption. This has been clearly demonstrated by William *et al.,* [131]. Adsorption of di-nitrophenol (DNP) and trichlorophenol (TCP) to the FT30-BW membrane was significantly less than that of benzene. However, they caused a much more severe flux decline. This is because benzene does not have any functional group that can form hydrogen bonding and can only adsorb to the membrane via non-specific adsorption. Both DNP and TCP have strong hydrogen bonding capacity. Therefore, they could possibly compete with water for hydrogen bonding sites (or hydrophilic groups) of the membrane polymer, resulting in severe flux decline [131]. Water flux decline was also found linearly correlated with the pK_a, a measure of hydrogen bonding capacity (see Figure 6.3).

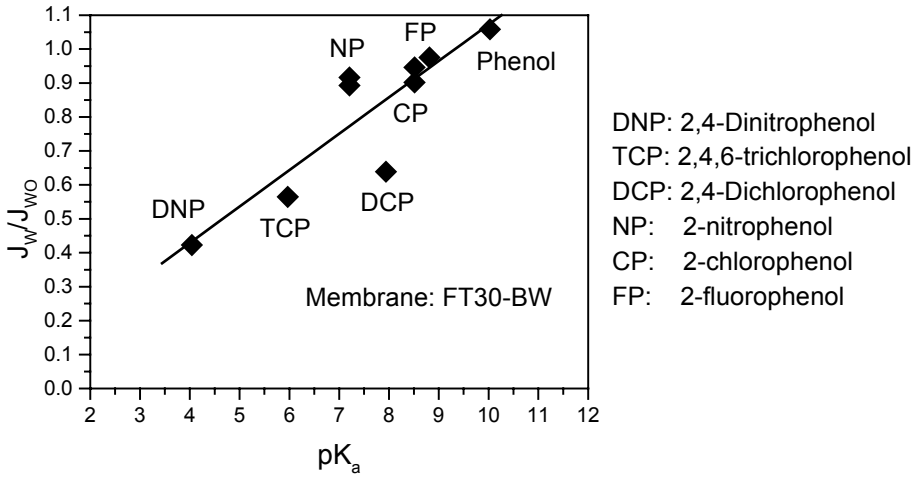


Figure 6.3: Water flux decline due to adsorption as a function of pK_a for selected phenolic compounds (adapted from [131]). Experiment conditions: applied pressure = 14 bar, temperature = 24 oC, feed concentration ranges from 0.2 to 0.5 mM.

Trace organics with some hydrogen bonding capacity are often hydrophobic at the same time. Furthermore, since water has a strong capacity as both a hydrogen donor and acceptor, water-trace organics interaction can interfere with the adsorption and desorption process, hindering studies of hydrogen bonding adsorption at trace concentration. In fact, hydrogen-bonding studies are often conducted under non-aqueous solution (which is probably more prevalent in biological cells) [221, 224, 225].

2.3.3 Electrostatic adsorption

Within the scope of this study, both entities of solute – membrane systems are essentially organic. Both the membrane functional groups and trace organics are neutrally or only weakly charged under typical conditions. While electrostatic interactions can be important in membrane retention of charged organics, they play a minor role in adsorption, probably with the exception of the dipole-dipole interaction. Van der Bruggen *et al.,* [214, 226] examined the correlation between adsorption of organic compounds to NF membranes and their dipole moments and reported a characteristic trend between rising adsorption and a increase in dipole moment of the organic compounds. The authors, however, expressed some reservation over the use of dipole moments as indicative parameter for adsorption to the membrane as dipole moments are usually measured in a non-aqueous solvent [214].

2.3.4 Factors influencing adsorption

As discussed above, adsorption of trace organic contaminants to NF/RO membranes depends on the physicochemical properties of both the membranes and solutes. Hydrophobicity of the membrane, or strictly speaking the availability of a hydrophobic domain within the membrane, plays an important role in hydrophobic interactions. This also includes the membrane surface roughness and its pore size. Hydrogen bonding capacity of the trace organics is essential in specific adsorption to the membrane. The dissociation constant pK_a can be used as indicator of the hydrogen bonding capacity. These factors are again strongly influenced by the solution chemistry such as pH and ionic strength. The hydrodynamic conditions in which filtration is carried out, such as pressure and recovery, can also affect on adsorption since they determine the transient condition of the adsorption process.

2.4 Adsorption models

Although adsorption studies in relation to membrane filtration are still limited, a vast amount of dedicated research has been devoted to adsorption study in general. Numerous models, both theoretical and empirical, have been developed to understand and present the adsorption isotherm. Most prevalent amongst them are the Langmuir and Freundlich models. Although empirical, the Freundlich model is widely used. It assumes an exponential decaying function of site density with respect to the enthalpy change during adsorption. Adsorption isotherm of the Freundlich model can obtained as:

$$\Gamma_{eq} = K \cdot C_{eq}^{1/n} \qquad (6.4)$$

where Γ_{eq} and C_{eq} are equilibrium concentration of the adsorbate (trace organic) in the solid phase (the membrane) and aqueous phase, respectively. K and 1/n are the adsorption capacity and adsorption intensity, respectively. Depending on 1/n, the adsorption isotherm can be concave, linear, or convex. Concave adsorption isotherm is unfavourable, as high concentration in the aqueous phase is needed for low adsorption to the solid phase. On the other hand, convex isotherm is favourable as low solute concentration in the solution can result in high adsorption. Linear adsorption isotherm occurs when 1/n approaches unity. It is quite common in very dilute solutions [227].

The Langmuir isotherm is the most widely used adsorption model for practical applications. Adsorption isotherm for pure component adsorption is defined as:

$$\Gamma_{eq} = \frac{\Gamma_{max} B \cdot C_{eq}}{1 + B \cdot C_{eq}} \qquad (6.5)$$

where Γ_{max} is adsorbed amount at saturation and B is called the Langmuir constant. At low solute concentrations, the isotherm reduces to a linear form, which is consistent with the phenomenon discussed above.

3. *Materials & Methods*

3.1 Membranes

Nine flat sheet NF/RO membranes — denoted as NF-270, TFC-SR1, TFC-SR2, TFC-S, TFC-ULP, ACM-4, TS-80, XN-40 and X-20 were selected for this study. Characteristics of these membranes have been described in detail in Chapter 3.

3.2 Selected trace organics

Seven notable endocrine disrupting chemicals (EDCs) were selected for this study, namely nonyl phenol (NP), tert butyl phenol (TBP), and bis-phenol A (BPA) presenting hormone mimicking compounds; and estrone (E1), estradiol (E2), progesterone (P), and testosterone (T) presenting natural steroid hormones. Once again, molecular weight and several other physicochemical properties including solubility in water, pK_a, and log K_{ow} of the selected EDCs have been described in detail in chapter 3.

3.3 Membrane filtration units and filtration protocols

Standard dead end and a cross flow filtration stirred cells were used in this study. The dead end stirred cell has been described in detail in Chapter 3. The cross flow filtration test unit – namely the Yale cross flow system, has also been described in detail in Chapter 3.

3.4 Static adsorption experiments

Static adsorption experiments (without an applied pressure) were performed in an automatic incubator shaker (Bioline, Edwards Instrument Company, Australia). A membrane area of 21.2 cm^2 was gently washed using MilliQ water as for the filtration experiment. Since estrone can approach the membrane from both sides, double the membrane area (42.4 cm^2) was used for calculation. The membrane was then cut into small pieces and placed in a conical flask. 50 mL of test solution containing 1 mM $NaHCO_3$, 20 mM NaCl at pH 8.0 and the required concentration of estrone was introduced to the flask. The flask was immediately placed into the shaker and 1 mL of sample was taken for every measurement as the experiment progressed. The flask was covered with nylon film to avoid evaporation and shaken at 100 rpm to ensure a homogeneous solution. A temperature of 25^oC was maintained throughout the experiment. Unless otherwise stated, initial concentration of hormone in the solution was 100 ng/L. At the end of the adsorption experiments, the membrane was placed into another flask containing background electrolyte solution (1 mM $NaHCO_3$, 20 mM NaCl, at pH 8.0, and with no estrone). The flask was also shaken at 100 rpm and 1 mL of sample was taken in specific time intervals to study the desorption behaviour of estrone.

For comparison, several static adsorption experiments were also carried out using the stirred cell. Hormone solution was constantly mixed in a stirred cell containing a NF-270 membrane sample without pressurization. 1 mL of sample was taken at specific time intervals for analysis.

3.5 Direct adsorption quantification

The extent of adsorption of estrone to the membranes was determined by the following procedure: at the end of each filtration experiment, the membranes were cut into small pieces and placed in a scintillation vial to which 5 mL of acetone was added. The vial was shaken vigorously and left for 1 hour for all estrone to dissolve. 1 mL of solution was then extracted into another vial which was air dried, redissolved with 1 mL of MilliQ water and 9 mL of scintillation liquid added prior to analysis.

3.5.1 Mass balance calculation

When adsorption of EDCs to the membrane has reached equilibrium, concentration in the permeate and concentrate can be quantified based on a simple mass balance equation. The membrane recovery and retention are defined in Eqs. 6.6 and 6.7, respectively.

$$\mathrm{Re}c = \frac{F_P}{F_F} \tag{6.6}$$

$$\mathrm{Re}t = 100 \times \left(1 - \frac{C_P}{C_F}\right) \tag{6.7}$$

where F_P, F_F, C_P, and C_F are feed flow rate, permeate flow rate, permeate concentration and feed concentration, respectively. From Eqs. 6.6 and 6.7, concentration in the permeate (C_P) and concentrate (C_C) can be expressed as:

$$C_P = \left(1 - \frac{\mathrm{Re}t}{100}\right) \times C_F \tag{6.8}$$

$$C_C = \frac{\left(C_F - C_P \times \mathrm{Re}c\right)}{\left(1 - \mathrm{Re}c\right)} \tag{6.9}$$

According to conservation law, the mass balance within the filtration system can be expressed as:

$$C_F \times V_F = C_C \times V_C + C_P \times V_P - Adsorption \tag{6.10}$$

Where V_F, V_C, V_P are volume or volume flow rate of the feed, concentrate, and permeate (streams), respectively.

The concentration of EDCs in spent membrane cleaning solution can be calculated as follows:

$$C_{Spent} = \frac{\Gamma \times A}{V} \tag{6.11}$$

where C_{Spent} is EDC concentration in the spent cleaning solution, Γ is the amount adsorbed to the membrane per meter square, A is the membrane area, and V is the cleaning solution volume.

4. *Adsorption and its implication to membrane filtration of trace organics*

4.1 Adsorption quantification

Assuming that the amount of estrone loss from the solution phase is equivalent to the amount of estrone adsorbed to the membrane, adsorption of estrone on the membrane can be calculated from mass balance considerations using Eq. (6.10). It can also be directly quantified by the analytical procedure described previously. All values obtained from the analytical measurement are plotted

against values obtained from the mass balance calculation in Figure 6.4. The overall difference between measured and calculated results is small. Indeed, an excellent correlation between analytically determined values and calculated values is observed. Where analytical and calculated values are found to be significantly different, we have assigned the extent of adsorption as the average of the two measured and calculated values.

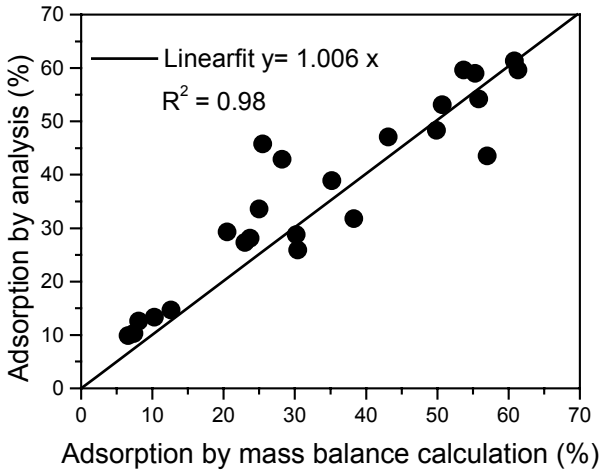


Figure 6.4: Adsorption - Analytical vs Mass Balance calculation - in NOM, FA and background buffer solutions.

4.2 Adsorption in natural water and secondary effluent

Estrone retention, adsorption and UV_{254nm} retention in natural water, in synthetic fulvic acid solution and in secondary effluent obtained from stirred cell experiments are shown in Table 6.1, Table 6.2, and Table 6.3, respectively. In general, TFC membranes adsorb more estrone than others. This is consistent with our previous contention as they are low resistance membranes and the flux is higher. Estrone adsorption in natural water and secondary effluent is similar and slightly lower than that in fulvic acid. FA is a purified reference material, while both secondary effluent and NOM are unpurified. Both contain low molecular weight acids, which may facilitate transport of estrone through the membranes, while larger compounds are retained and may increase retention due to trace organic–NOM interaction. The presence of matrix compounds such as organic matter may influence the composition of the boundary layer. Partition into such organic constituents may also influence the back diffusion of estrone into the bulk solution. It is noteworthy that the permeate fluxes of the X-20, ACM-4, and TS-80 membranes are significantly lower than those of the others. Consequently, these membranes are subjected to a lower concentration polarization, which can possibly explain a lower estrone adsorption as can be seen in Table 6.1, Table 6.2, and Table 6.3.

However, while adsorption changes considerably due to the presence of organics in the feed solution, retention does not respond to the same extent. According to a model on the transport of small molecules penetrating into dense membranes due to diffusion developed by Chen *et al.* [228], transport behaviour can be classified into three categories: (i) Fickian diffusion, in which the rate of diffusion is much less than that of sorption; (ii) sorption control process, in which the diffusion rate is much faster than that of sorption; and (iii) non-Fickian or anomalous diffusion, which occurs when the diffusion rate and the sorption rate are comparable. It is unlikely that sorption control process and non-Fickian diffusion dominate as considerably high retention and adsorption can be observed in all experiments (see Table 6.1, Table 6.2, and Table 6.3). If the sorption control process or non-Fickian diffusion occurs, an increase in adsorption leads to a decrease in retention [228]. It appears that the transport of hormone through the membrane follows a typical Fickian model, although one can expect that transmembrane pressure may increase the diffusion rate and at an adequate pressure non-Fickian diffusion may occur.

Table 6.1: Adsorption & retention in NOM solution (10 mgL^{-1} NOM as organic carbon, pH 7.8, 20 mM NaCl, 1 mM $NaHCO_3$, 0.5 $CaCl_2$)

Membrane Type	Ca/Na Retention (%)	J_F/J_{W0}	Estrone Retention (%)	Estrone Adsorption (ng/L)		UV_{254nm} Retention (%)
				Analytical Measure	Mass-Balance Calculation	
TFC-ULP	58/47	0.80	90	8.0	8.7	94
TFC-S	88/73	0.68	94	5.6	4.8	96
TFC-SR1	55/24	1.09	96	11.3	11.3	97
TFC-SR2	68/31	1.00	88	10.3	10.0	98
X-20	95/91	0.72	96	1.2	1.8	99
ACM-4	96/92	0.95	97	1.5	2.3	99
XN-40	40/27	0.87	73	7.1	5.9	97
TS-80	95/88	0.74	97	1.9	2.5	99

Large natural organic molecules can deposit onto the membrane surface causing flux decline and increase in solutes retention [229, 230]. However, as the membrane, natural organics and fulvic acid are all negatively charged, minimal deposition of organics is expected to occur due to the electrostatic repulsion between the membrane surface and the organic matter. Some extent of flux decline is observed, but it is mostly because of osmotic pressure effects due to salt retention. Organic matter influences charge and hydrophobicity of the membrane, thus adsorption of micro-contaminants on the membrane. Adsorption of estrone on the most hydrophilic TFC-SR1 and TFC-SR2 membranes is consistently high at approximately 10.5 ng, corresponding to about 60% of the

initial mass in the feed solution. Note that a similar pattern was observed for the MilliQ and buffer matrices. It appears as though adsorption for those membranes is independent of the matrix compounds indicating a strong affinity. Consistently, XN-40 showed the lowest estrone retention, although adsorption is reasonably high. This is possibly because XN-40 has fewer interactive sites for adsorption and the largest pores, so molecules can pass through the membrane without a very close contact with the pore surface. For other membranes, although retention is similar in general, adsorption is found to vary depending on the matrix compounds.

Table 6.2: Adsorption & retention in FA solution (10 mgL^{-1} FA as organic carbon, pH 7.8, 20 mM NaCl, 1 mM $NaHCO_3$)

Membrane Type	Na Retention (%)	J_F/J_{W0}	Estrone Retention (%)	Estrone Adsorption (ng/L)		UV $_{254nm}$ Retention (%)
				Analytical Measure	Mass-Balance Calculation	
TFC-ULP	62	0.76	90	10.6	8.1	97
TFC-S	80	1.00	96	6.5	7.2	98
TFC-SR1	25	1.22	95	10.2	10.9	99
TFC-SR2	37	1.13	87	11.3	11.0	98
X-20	80	0.73	98	3.8	7.0	98
ACM-4	65	0.78	98	4.3	8.7	96
XN-40	24	0.97	76	9.2	8.9	98
TS-80	93	0.80	94	2.3	2.7	98

Table 6.3: Adsorption & retention in secondary effluent

Membrane Type	Ca/Na Retention (%)	J_F/J_{W0}	Estrone Retention (%)	Estrone Adsorption (ng/L)		UV $_{254nm}$ Retention (%)
				Analytical Measure	Mass-Balance Calculation	
TFC-ULP	84/72	0.90	97	-	8.2	97
TFC-S	98/85	0.77	99	-	2.6	96
TFC-SR1	75/34	1.19	93	-	10.6	97
TFC-SR2	40/8	1.02	86	-	10.5	85
X-20	94/86	0.91	92	-	3.3	92
ACM-4	89/82	0.62	77	-	3.7	96
XN-40	60/38	0.87	78	-	6.6	84
TS-80	95/82	0.82	91	-	2.6	94

The fact that both size exclusion and adsorption (and subsequent diffusion) are prevalent removal mechanisms can significantly hinder any attempts to correlate adsorption to retention. It is noteworthy that data presented in Table 6.1, Table 6.2, and Table 6.3 were obtained from dead-end stirred cell filtration experiments. Much longer experimental time is required to examine the effects

of adsorption and membrane pore size on retention. As adsorption is the primary concern in this chapter, results of such experiments are presented in the next chapter.

4.3 Adsorption isotherm

The adsorption isotherms of TFC-SR2 and X-20 membranes are obtained using static adsorption experiments and are presented in Figure 6.5. While the adsorption isotherms of the two membranes are linear, which is common in very dilute system [227], partition coefficients are significantly lower, 8.1 and 4.0 for TFC-SR2 and X-20 membranes, respectively.

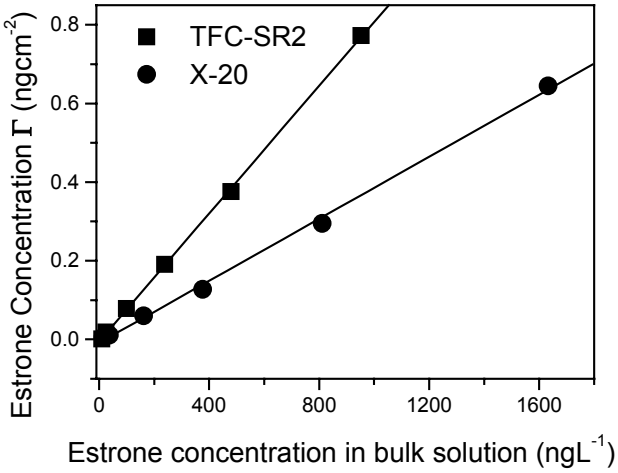


Figure 6.5: Adsorption isotherm of TFC-SR2 and X-20 (static adsorption experiment, 1 mM $NaHCO_3$, 20 mM NaCl, and pH 8.0).

Diffusion is the only driving force in static adsorption process. Due to the small pore size of the active layer, hydraulic resistance reduces the penetration of estrone and adsorption occurs mainly at the surface. Consequently, a much smaller amount of estrone is adsorbed as can be observed in the static adsorption experiments. The difference in partition coefficients of the TFC-SR2 and X-20 membranes can be attributed to the fact that pore size of the X-20 membrane is smaller than the estrone molecule and adsorption at the surface dominates. Hydraulic resistance hinders the convection of water into the membrane and hence the transport of trace organics to the adsorptive sites within the membrane pores. Although it is possible for the supporting layer to adsorb estrone, results reported here also indicate that the active layer indeed dominates the adsorption process.

Estrone adsorption as a function of feed concentration (1, 10, 100, and 1000 ngL^{-1}) for TFC-S and TFC-SR2 membranes in filtration experiment are presented in Figure 6.6. Both membranes show a linear curve with a similar partition coefficient K of 48 Lm^{-2}. During the filtration process, since the

pore size of TFC-S and TFC-SR2 is similar or larger than the estrone molecule, hydraulic resistance is overcome by convection. The membrane average pore radius is 0.37 and 0.64 nm for the TFC-S and TFC-SR2 membranes, respectively, whereas the Stokes radius of estrone is 0.40 nm. Consequently, estrone can penetrate into the membrane active layer, where site-specific adsorption can occur presumably via hydrogen bonding.

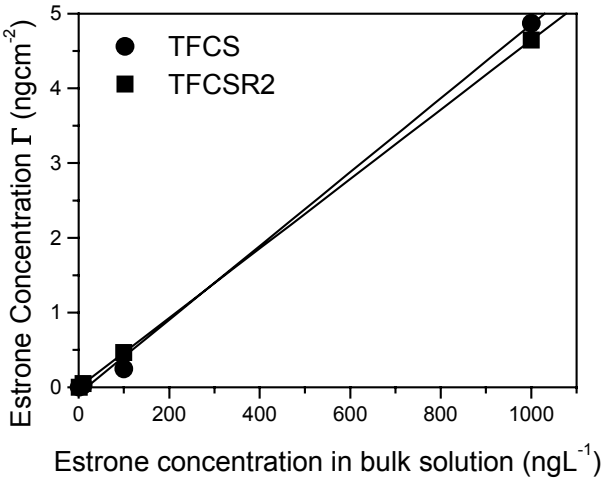


Figure 6.6: Adsorption to the TFC-SR2 and X-20 membranes as a function of feed concentration (filtration experiment, 1 mM $NaHCO_3$, 20 mM NaCl, and pH 8.0).

Pore size of the supporting layer is in the order of 100 nm [131], thus, hydraulic resistance is expected to be negligible and the partition coefficient obtained in filtration and static adsorption experiment would be similar if adsorption to the supporting layer dominates. This is consistent with the results reported by William and co-workers [131] who found that the majority of trichlorophenol was adsorbed by the active layer of the FT30-BW membrane (polyamide on polysulfone support) and subsequent flux decline was observed as an indication of site specific adsorption. However, flux decline could not be observed in our experiments due to the very low concentration of estrone.

4.4 Adsorption & desorption kinetics

The results from the study of the adsorption kinetics are shown in Figure 6.7. After about 200 minutes the adsorption of estrone by the TFC-SR1, TFC-SR2 and XN-40 had attained the plateau value, while this takes significantly longer for the TS-80, ACM-4 and X-20 membranes. Despite the fact that all membranes are made of the similar polymer, this indicates some differences in physical characteristics of the membrane.

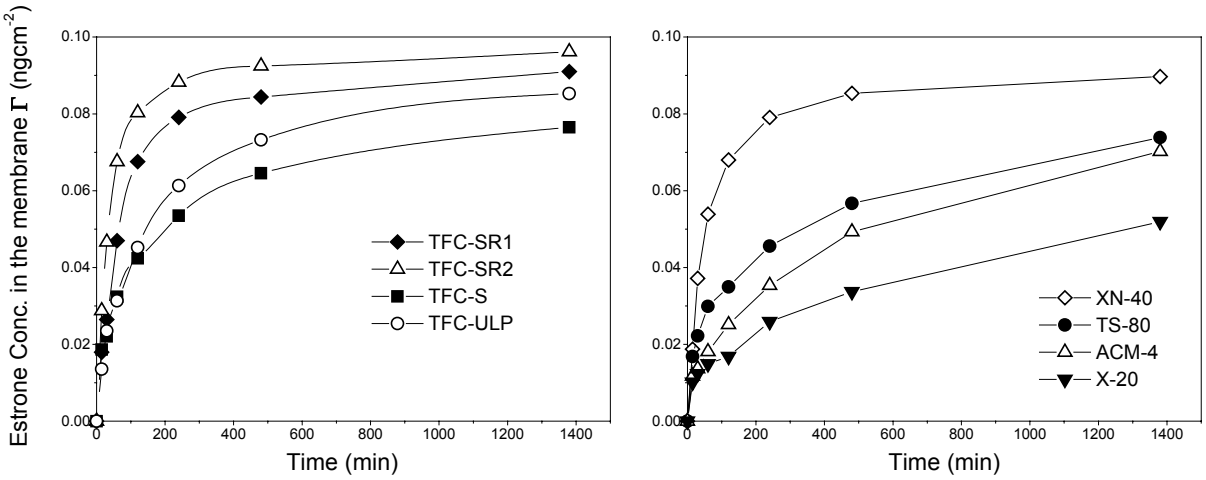


Figure 6.7: Adsorption kinetics (static adsorption experiment, 1 mM $NaHCO_3$, 20 mM NaCl, 100 ng/L estrone and pH 8.0).

Unlike adsorption kinetics, desorption kinetics of all membranes follow the same pattern and reach equilibrium at 200 minutes. However, considering adsorption isotherms of the TFC-SR2 and X-20 membranes (see Figure 6.5), it can be seen in Figure 6.8 that the desorption process is not complete, which may present an irreversible factor at this experiment condition.

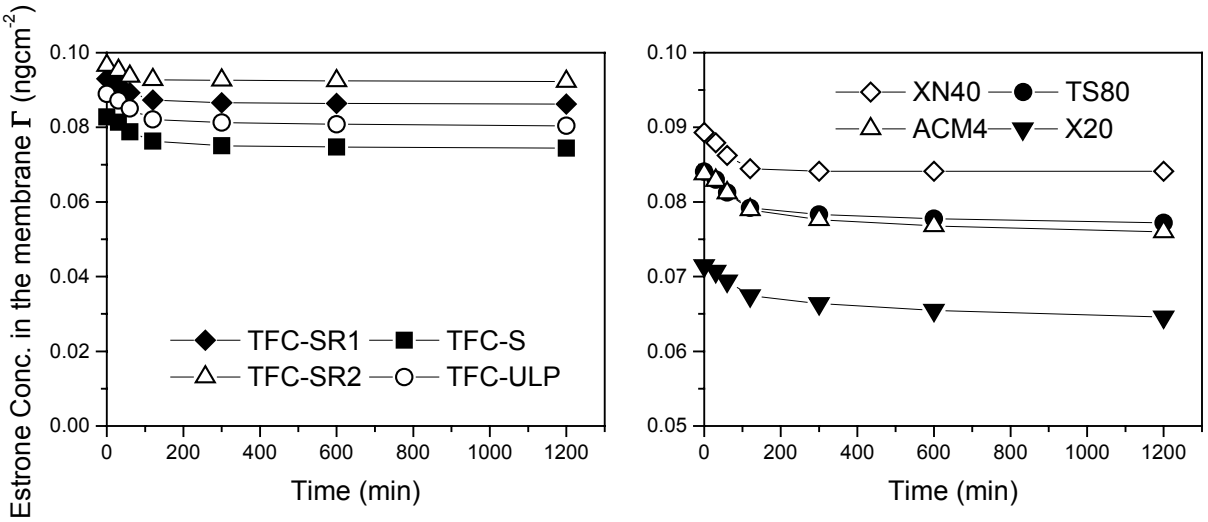


Figure 6.8: Desorption kinetics (static desorption experiment, 1 mM $NaHCO_3$, 20 mM NaCl, 100 ng/L estrone and pH 8.0).

4.5 pH and ionic strength effects

Batch filtration experiments were performed to investigate the effect of solution chemistry (pH and ionic strength) on the adsorption of estrone. A new membrane coupon was used for each pH and ionic strength concentration. Adsorption in nanograms (10^{-9} g) of estrone per membrane surface

area (cm^2) from a 100 ngL^{-1} solution by TFC-SR2, TFC-S and X-20 membranes as a function of pH is shown in Figure 6.9. Variation in pH of the solution can result in conformational changes of the estrone molecule or the electrostatic interaction between estrone and the membrane surface, which will ultimately influence estrone adsorption onto the membrane. A slight reduction in adsorption as pH increased at pH below the dissociation constant of estrone (pK_a = 10.4) indicates that some degree of hydrophobic adsorption may exist, although the trend is too minor to draw any conclusive statements. For TFC-SR2 and TFC-S membranes, estrone adsorption decreases dramatically as the pH exceeds the pK_a value of estrone, which suggests that site-specific adsorption plays a more importance role in this case. Estrone adsorption by the X-20 membrane is considerably less than that by TFC-S and TFC-SR2 membranes. Consequently, a sudden reduction in adsorption when pH exceeds the pK_a value of estrone was not observed in this membrane. As proposed in earlier work, when dissociated, estrone loses its proton and become a negative species; it is unable to form hydrogen bonding with the membrane functional groups, resulting in a sudden reduction in adsorption [124]. More gradual reductions in hydrophobic adsorption of bovine serum albumin (BSA) on regenerated cellulose membrane when pH exceeds isoelectric point (IEP) of BSA was observed by other researchers [217].

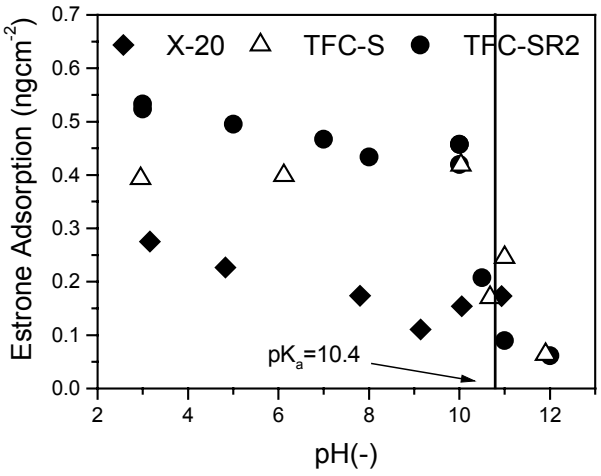


Figure 6.9: Adsorption of estrone as a function of pH (TFC-SR2, TFC-S, and X-20 membranes,1 mM $NaHCO_3$, 20 mM NaCl).

Figure 6.10 shows estrone adsorption from a 100 ngL^{-1} feed solution onto a TFC-SR2 membrane as a function of NaCl concentration at pH near neutral. The ionic strength, or NaCl concentration may partially screen electrostatic potentials and polarity. While modification of molecular structure is important for large molecules, the effect with estrone is likely to be minimal. Similarly, the ionic strength may reduce the electrostatic interaction between the molecules and the surface functional

groups of the membrane. Both phenomena can influence hydrophobic interactions between the estrone molecule and the membrane surface. Although there is some variation in adsorption as NaCl concentration varies from 0 to 100 mM, the variation is likely within experimental error. This further indicates that site-specific interaction also plays a major role in the adsorption processes.

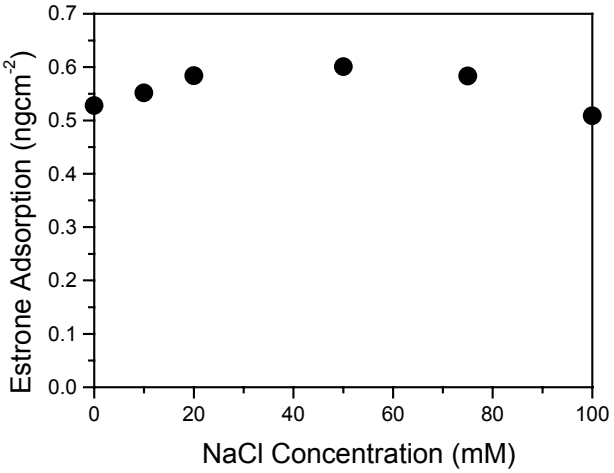


Figure 6.10: Adsorption of estrone as a function of NaCl (TFC-SR2 membrane, 1 mM $NaHCO_3$ and pH=8.0).

Retentions of estrone by TFC-SR2 as a function of pH and NaCl concentration resembled the curve presented in Figure 6.9 and Figure 6.10. High estrone retention (above 90%) at low pH and low estrone retention (about 55%) clearly indicate that retention in this case was mainly governed by adsorption. Drop in adsorption resulted in a milder decline in retention of estrone by the TFC-S membrane, whereas no decline in retention of estrone by the X-20 membrane was observed when estrone adsorption decreased. As the membrane pore size is in the order TFC-SR2>TFC-S>X-20, these results show that effect of adsorption on retention of estrone by NF/RO membranes can be pore size dependent.

4.6 Breakthrough observations

Variation in water recovery and subsequent concentration factor can also induce the release of steroid hormones. To study this possibility, estrone retention by dead end filtration was compared to that by crossflow filtration using the TFC-S membrane. Dead end filtration experiments were conducted with a series of fresh feed solutions using the same membrane sample. A crossflow filtration experiment was conducted using a SEPA® cell (Osmonics, USA). Hormone adsorption took place until adsorption/desorption within the membrane had been equilibrated. Consequently, distinct breakthrough curves (see Figure 6.11), as often seen in activated carbon adsorption or ion exchange of other contaminants were observed in both dead end and cross flow filtration

experiments. In both cases, the permeate concentration of the TFC-S membrane became stable below the feed concentration, which indicates some degree of retention due to a steric interaction mechanism. However, due to a concentration build-up at the membrane surface and ineffective back diffusion during dead end filtration, the permeate concentration by this configuration was much higher than that of cross flow filtration. Results reported here indicate that increasing recovery (which reflects a move from cross flow to more dead end type filtration) may cause a substantial increase in permeate concentration of steroid hormones. This is important for risk management where retention of micro-pollutants such as hormones is essential.

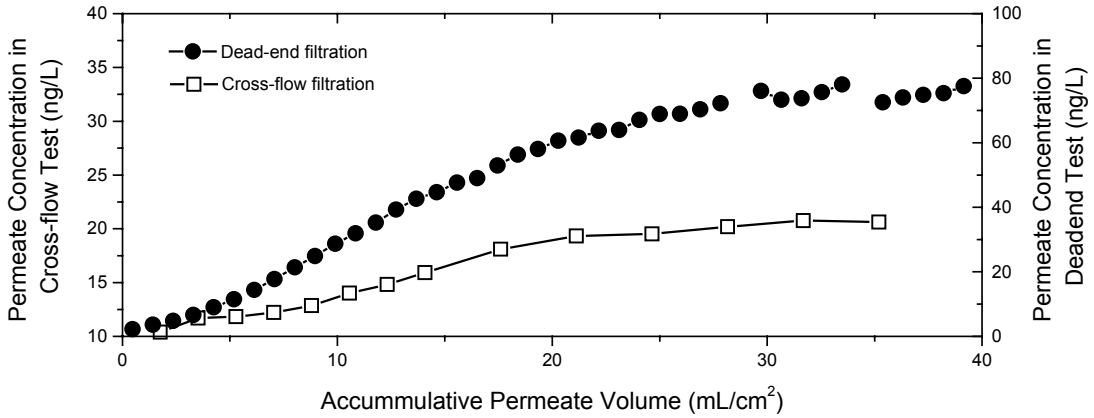


Figure 6.11: Permeate concentration of estrone in dead end and crossflow filtration with the TFC-S membrane as a function of permeate volume (feed solution: 100 ng/L estrone, 1 mM $NaHCO_3$, 20 mM NaCl, and pH 8.0).

4.7 Release of trace organics from the membranes

The accumulation of trace organics on a NF membrane and subsequent release was simulated. Estradiol and progesterone solutions were constantly agitated in a stirred cell containing a NF-270 membrane sample without pressurization. Hormone concentration in the stirred cell at a specified interval is presented in Figure 6.12. As there is no applied pressure and the solution does not have contact with the membrane's supporting layer, the result indicates that the membrane's active layer can accumulate a significant amount of trace organics. At the end of the static adsorption experiment, estradiol and progesterone concentrations in the cell were 62 ng/L and 47 ng/L, respectively.

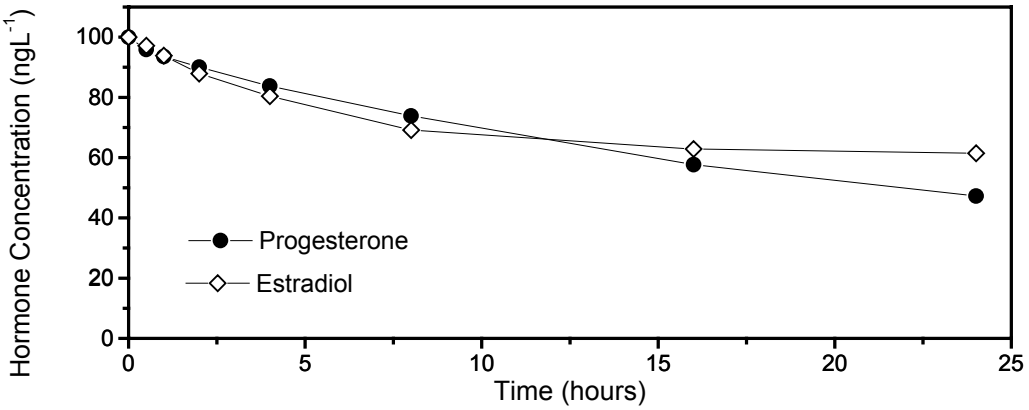


Figure 6.12: Static adsorption of estradiol and progesterone to the NF-270 membrane (feed solution: 100 ng/L hormone, 1 mM $NaHCO_3$, 20 mM NaCl, and pH 8.0).

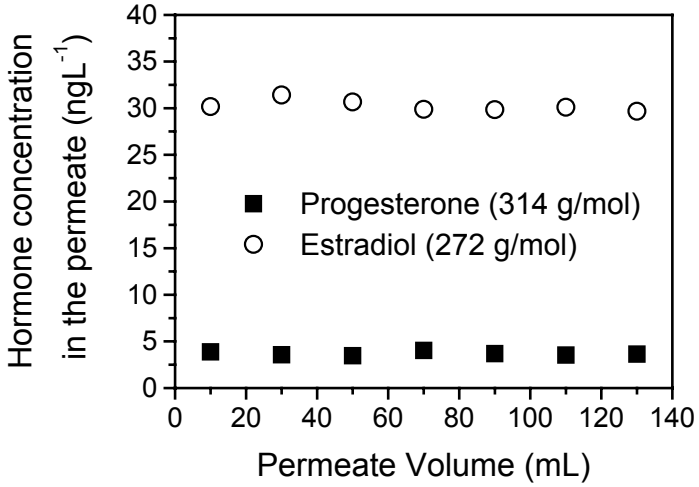


Figure 6.13: Permeate concentration of estradiol as a function of permeate volume after pre-adsorption (NF-270 membrane, P=4.5 bar, feed solution: 1 mM $NaHCO_3$, 20 mM NaCl, and pH 8.0).

Since the adsorption (or partitioning) process was accomplished via a weak form of secondary bonding, desorption and adsorption can simultaneously occur. At the completion of the static adsorption (see Figure 6.12), the depleted feed solution was filtered through the NF-270 membrane under a pressure of 4.5 bar (60 psi). Given that the average pore radius of the membrane is 0.41 nm (see Chapter 4) and the Stokes radius of estradiol is estimated to be 0.40 nm [174, 231], high estradiol concentration in the permeate (see Figure 6.13) clearly indicates that estradiol which is previously partitioned to the membrane desorbs to the permeate. A much lower permeate concentration of progesterone is observed since it has a larger MW, corresponding to a larger Stokes radius of 0.43 nm. It has been shown in Chapter 4 (and will be further discussed again in the next chapter) that steroid hormones after being adsorbed to the membrane surface can diffuse through a very thin layer of the nanofiltration active skin. Furthermore, a high concentration gradient due to the adsorption (or partitioning) of steroid hormones to the membrane can also

contribute to this diffusion. This diffusion process depends on the solute diffusivity and also on the polymer density and skin layer thickness of the membranes; therefore, it may be lessened for dense RO membranes that usually have a much thicker active skin layer. However, it is possible that the membranes can act as a reservoir for EDCs and release compounds back into the concentrate stream, resulting in an erratic concentration of EDCs in the concentrate.

4.8 Membrane cleaning & trace organic accumulation in cleaning solutions

In practice, NF membranes are regularly cleaned by a cleaning solution that has a pH of around 11 and usually consists of caustic soda combined with surfactant such as EDTA or sodium dodecyl sulfate and enzyme cleaners. However, given the pK_a values of several EDCs as presented in Chapter 3, they can dissociate and become negatively charged at this pH (see Figure 6.14 as an example for estradiol) and a significant amount of EDCs can desorb into the cleaning solution. To test this hypothesis, at the completion of the static adsorption of estradiol to the NF 270 membrane (at pH 8), the depleted feed solution was replaced by a background solution containing no estradiol. The pH of this background solution was 11. A pressure of 4.5 bar (60 psi) was then applied. Estradiol concentration in the permeate samples is presented in Figure 6.15. As can be seen in Figure 6.15, desorption of estradiol at pH 11 occurs instantaneously. Estradiol concentration in the permeate decreases as estradiol is desorbed from the membrane polymer matrix. In practice, cleaning is usually performed at high cross flow velocity with negligible transmembrane pressure. Although the possibility that EDCs can desorb into the permeate side of the membrane during cleaning in minimal, results reported here clearly imply that wastewater obtained from the cleaning process may contain a significant amount of EDCs, which should be taken into account for later disposal. It is further possible that permeate will contain a higher concentration of EDCs as filtration recommences.

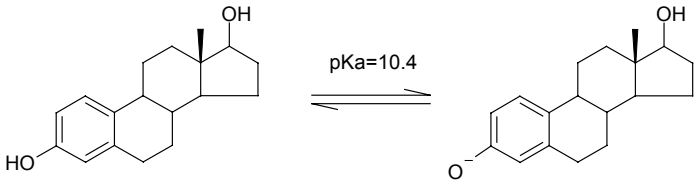


Figure 6.14: Speciation of estradiol as pH exceeds pK_a value of the compound.

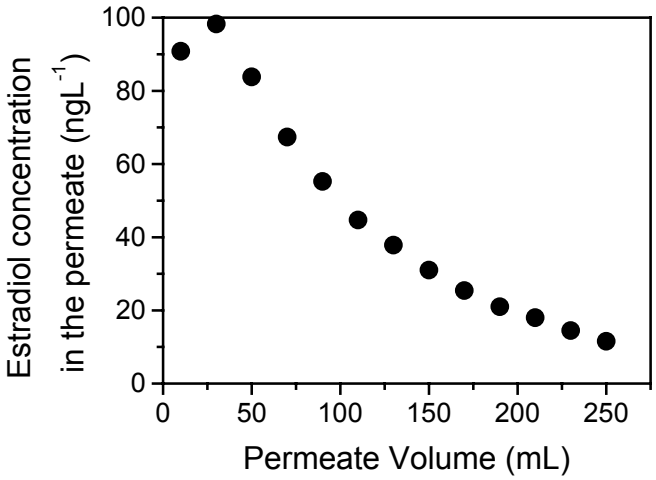


Figure 6.15: Permeate concentration of estradiol as a function of permeate volume after pre-adsorption (NF-70 membrane, P=4.5 bar, feed solution: 1 mM $NaHCO_3$, 20 mM NaCl, no estradiol, and pH 11.0).

4.9 Adsorption of different trace organic to the membrane

Since adsorption of trace contaminants to the membrane will entail subsequent risk of break through, as demonstrated in section 4.6, which has implications on the treatment and disposal of spent cleaning solution, it is essential to quantify the amount that may adsorb to the membrane. Lab-scale cross flow filtration experiments were carried out with small membrane samples to determine the adsorbed amount of endocrine disrupting chemicals (EDCs) to the membranes. Adsorbed amounts were calculated using mass balance when membrane saturation had been achieved, which is after approximately 24 hours in typical experiments. Adsorption of EDCs used in this study (per one square meter) to the NF 270 membrane is presented in Figure 6.16. Results are expressed in μg or ng per m^2 of membrane. The hormone mimicking compounds adsorbed significantly more to the NF 270 membrane than the natural steroid hormones due to the fact that the initial hormone mimicking compound concentration was 6,000 times higher than that of steroid hormones (which corresponds to the levels found in wastewaters). Although all EDCs in this study have quite similar $\log K_{ow}$ value, ranging from moderate to high, there is a weak correlation between the amount of EDCs adsorbed to the NF-270 membrane and their $\log K_{ow}$ values. This indicates that adsorption is driven by hydrophobic interactions to a certain extent. Apart from $\log K_{ow}$, other physicochemical parameters of the organic solute such as dipole moment and dielectric constant may also influence adsorption [226], but are difficult to obtain for such compounds.

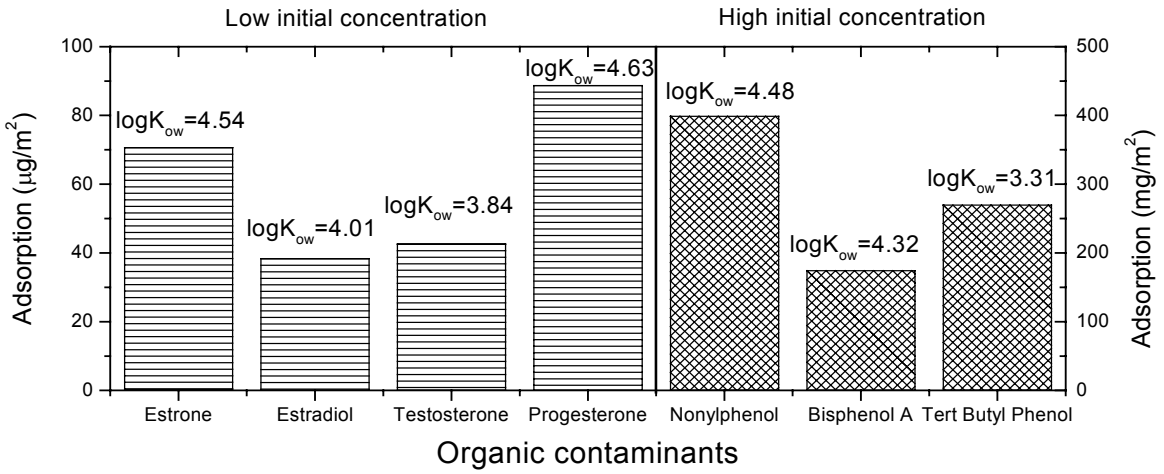


Figure 6.16: Estimated adsorbed amount of trace contaminants to the NF 270 membrane. Saturation was achieved after approx. 24 hours cross flow filtration. Initial solution concentration for steroid hormones 100 ng/L or hormone mimicking compounds 600 μg/L in a background solution containing 20 mM of NaCl, and 1 mM of $NaHCO_3$, pH ~ 8.0.

Initial concentrations used in this study probably present a worst case scenario as treated effluents and environmental concentrations of these contaminants can be significantly lower, typically in the range of 1 ng/L or less [36, 87, 232]. However, considering the amounts adsorbed reported in Figure 6.16, there is potentially a considerable risk of EDCs release from the membrane during cleaning or erratic operating conditions. This is particularly the case when considering that a concentration of only 1 ng/L of estradiol can show a distinctive endocrine disrupting effect on fish. Other toxicological effects are largely unknown and may increase with the presence of a synergetic mixture of compounds [233]. The membrane area in a typical 8-inch module used in large scale applications is approximately 37 m^2. If released, the amount of estradiol adsorbed to 10 membrane modules would hence be sufficient to contaminate a water volume of 140,000 ML at 1 ng/L concentration, equivalent to the entire daily output of the Mery Sur Oise treatment plant – the world's largest nanofiltration plant for drinking water production, although small quantities of highly contaminated water may also be of concern. It must be emphasised that this is a relatively new and difficult issue, which is at present, highly debated in the field.

4.10 Fate of EDCs in NF/RO filtration processes

Membrane filtration is purely a physical separation process, which separates contaminants from the solvent (water) and transfers them to the concentrate. Concentrate treatment and subsequent disposal have therefore become an essential issue [234], particularly when it involves trace contaminants of concern such as EDCs. A schematic diagram showing estimated estrone concentration in the feed, permeate, concentrate, and spent membrane cleaning solution is shown in

Figure 6.17. These concentrations are in agreement with pilot scale experimental results reported previously [235]. It is noteworthy that the actual process may be complicated by adsorption (and desorption) of EDCs to (and from) the membrane. In this case, it is assumed that there is sufficient filtration time before membrane cleaning for the partitioning process to reach equilibrium. In practice, it is expected that concentrate concentration would increase gradually as the membrane adsorptive capacity is reduced. Concentrate concentration reaches a value as estimated in Figure 6.17, when the membrane adsorptive capacity has been exhausted. As discussed in section 4.7, complete desorption may occur during membrane cleaning with a high pH solution. EDC concentration in the concentrate (and to a limited extent in the permeate) may exhibit a cyclic pattern in accordance to the cleaning regime.

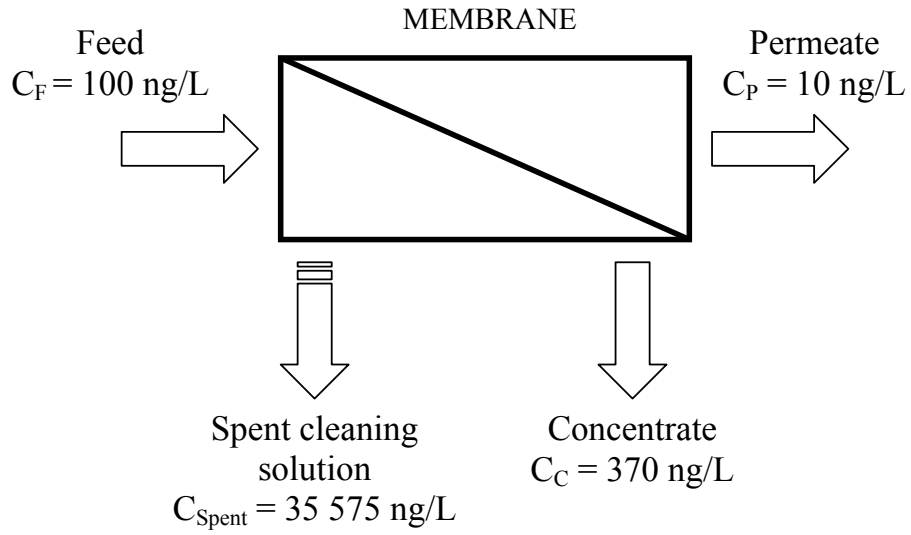


Figure 6.17: Estimated concentration of estradiol in different streams for assumed values of 90 % retention, recovery 75 % and cleaning solution volume of 40 litres per one 8-inch membrane element with a membrane area of approximately 37 m^2. Adsorbed amount of estradiol to the membrane at saturation is taken from Figure 6.16 (for the NF 270 membrane). Estradiol concentration in the spent solution was calculated using Eq. 6.11.

EDC concentration in the spent cleaning solution depends largely on the amount of EDC adsorbed to the membrane prior to cleaning and also on the volume of the cleaning solution. The cleaning solution volume for a spiral wound element should be at least adequate to fill in the volume of the membrane vessels, filters, and piping, which again depends on system arrangement. A typical cleaning solution volume required for one 8-inch membrane spiral wound element is approximately 40 liters [236]. This value is used in this study to estimate the concentration of EDCs in spent membrane cleaning solution. As demonstrated in Figure 6.17, EDC concentration in the spent cleaning solution can be extremely high. Furthermore, it is a common practice to reuse the cleaning

solution over a number of membrane vessels. Hence, EDC concentration in the spent cleaning solution may be even higher than estimated here. Although as mentioned earlier this probably presents a worst case scenario, due care should be dedicated to the treatment and disposal of spent membrane cleaning solution.

5. *Conclusions*

Adsorption is inherent in any NF/RO membrane filtration process, particularly when trace organics are involved. In this chapter, it has been demonstrated that simple mass balance can be used to quantify adsorption of trace organics to the membranes. Linear adsorption isotherms are observed during both static (no applied pressure) and filtration adsorption experiments. This is typical for a very dilute system. Under a static condition, desorption occurs marginally, however, under a typical transmembrane pressure, significant desorption to the permeate side can be observed in loose NF membranes, which have larger pore size than the trace organics. It appears that adsorption is strongly influenced by the solution pH and to a lesser extent by the presence of other organics in the bulk solution. On the other hand, ionic strength seems to have a negligible effect on adsorption.

Results reported here also demonstrate that the membrane can serve as a considerable reservoir for EDCs and their release can be possible during membrane cleaning or erratic pH variation during operation. Complete desorption of EDC to the membrane cleaning solution can occur at high pH. This may result in an extremely high concentration of EDCs (given it endocrinologically active dosage) in the spent cleaning solution. Treatment of the concentrate and the spent membrane cleaning solution should be carefully considered when EDCs are amongst the target contaminants in NF/RO membrane filtration. These results have a very important value as to date risk implications in association with concentrate and membrane cleaning solution disposal have not been adequately addressed.

Chapter 7

Sorption-diffusion

1. *Introduction*

It is universally accepted in the scientific world that any microscopic particles suspended in any gas or liquid and any dissolved ions in any solution are subjected to Brownian force. Indeed, due to Brownian motion, such microscopic particles or ions constantly make random and very small movements without any predefined direction. When there is a differential concentration, because there are more particles or ions from the more concentrated area, there is a net transfer of particles or ions to the less concentrated area. This very fundamental diffusion process has become a well-known transport phenomenon. In fact, diffusion can even happen in crystalline solids and the phenomenon can be strikingly similar [237], although the diffusive rate or net transfer of atoms can be much smaller.

Diffusion is often depicted by an analogy of a "random walk" [237, 238]. Various mechanisms, including interstitial and vacancy, have been hypothesised to explain the diffusion in crystalline solids [237]. Common amongst them is the prerequisite that atoms can move from one equilibrium position to the next in a random fashion, which eventually give rise to diffusion.

Although sorption-diffusion of organic solutes is rarely mentioned in membrane filtration texts, it is in fact the most widely accepted explanation of water transport in reverse osmosis (RO) membranes. Since RO membranes are commonly regarded as dense and nonporous, transport of water through the membrane is thought to happen via sorption-diffusion. This model assumes that the applied pressure is constant within the membrane at the high-pressure value and the applied pressure results in a concentration gradient of water in the membrane polymeric matrix. Application of the sorption-diffusion model has also been extended to dissolved salts due to the apparent ion-exchange capacity of some RO membranes. However, application of this model to nanofiltration (NF) membranes is rather limited. This is attributed to the fact that NF membranes are porous and pore flow or hydrodynamic models are much more prevalent for this membrane. Nevertheless,

some membrane researchers argue that a transition between a pore-flow and a sorption-diffusion mechanism can occur with NF membranes (pore size in the range of 0.5 to 1 nm in diameter) [222]. In other words, the transport phenomena can be explained by a sorption-diffusion mechanism for some solutes while a pore flow mechanism can be used for the others. With the emerging challenge to remove various types of trace organic contaminants in water and wastewater by membrane filtration, it is essential to examine the validity of the sorption-diffusion mechanism in explaining the transport of trace organics in membrane filtration processes.

Evidence of sorption-diffusion transport of organic solutes in dense membranes was first reported by Groß and Heintz [239, 240]. In addition to their findings, as can be seen in Chapter 6 and several other studies, trace organics such as natural steroid hormones and hormone mimicking compounds can adsorb (or partition) to polymeric membranes to a significant extent [9, 92, 136]. This can possibly be seen as indirect evidence of the sorption-diffusion of trace organics in membrane filtration processes. In Chapter 4, further evidence of the sorption-diffusion transport of such trace organics was revealed by comparing their retention to the predicted retention, based on a steric hindrance pore model. It is noteworthy that the findings also exemplified the NF membrane in a transition between a pore flow and a sorption-diffusion mechanism as mentioned above.

In addition to evidence from literature, this chapter aims to further strengthen the evidence of the sorption-diffusion mechanism with regard to the transport of trace organics in NF membrane filtration processes. Diffusion experiments were carried out with the natural hormone estrone, using a dialysis cell. The membrane active layer thickness was measured using a novel ion beam analysis technique and was subsequently related to the diffusion process of estrone. Diffusion coefficient of estrone in polymeric phase was determined and related to the membrane properties as well as the physicochemical characteristics of estrone. Possible diffusion mechanisms and the effects of diffusion on retention are described and discussed.

2. *Theory*

2.1 Stationary diffusion

There is an obvious analogy between heat conduction and diffusion of substance as both are due to random motions. Fick was the first to recognise this and applied the mathematical solution of a heat transfer problem to diffusion. In an isotropic medium, it is assumed that the rate of transfer of a diffusing substance through the unit area of a section is proportional to the concentration gradient normal to that section:

$$J = D \cdot \frac{C_{mI} - C_{mII}}{\Delta x} = D \cdot \frac{\partial C}{\partial x} \qquad (7.1)$$

where J is the flux of solute (diffusing substance), D is the diffusion coefficient in the membrane, and $\partial C/\partial x$ is the concentration gradient. Eq 7.1 is universally known as Fick's first law of diffusion. C_{mI} and C_{mII} are the concentration of the solute in the polymer membrane at the boundary with the concentrated solution and diluted solution respectively as depicted in Figure 7.1.

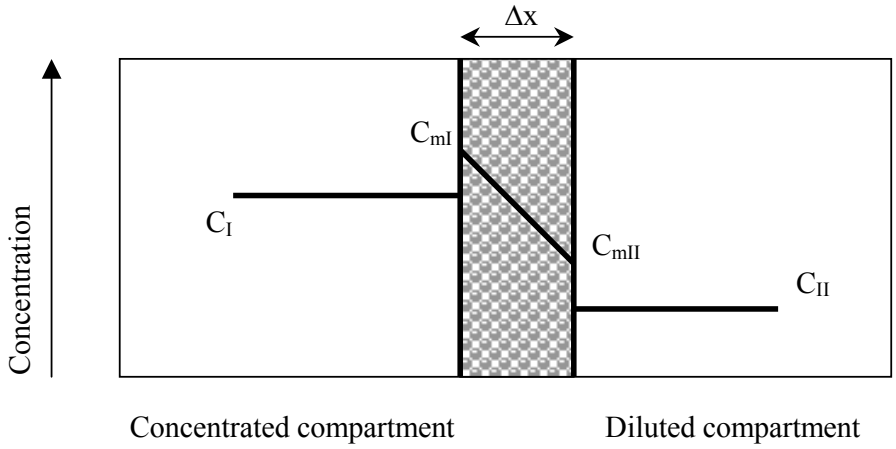


Figure 7.1: Schematics of the concentration profile of diffusing substance in a dialysis cell.

In a dialysis system where substance from a concentrated compartment (of volume V_I) diffuse through a membrane with an area of A into the other compartment (of volume V_{II}) with no initial concentration of such substance, the increase in concentration of the diluted compartment can be expressed as:

$$\frac{\partial C_{mII}}{\partial t} = \frac{J \cdot A}{V_{II}} \qquad (7.2)$$

Given a constant partitioning coefficient between the membrane and aqueous phase, one can relate membrane concentration at the membrane/liquid interface with the aqueous concentration in the bulk solution by:

$$C_m = S \cdot C \qquad (7.3)$$

where S is the partitioning (or solubility) coefficient between the membrane phase and the aqueous phase and subscript m is used to indicate the membrane phase. If the amount of solute in the aqueous phase is substantially larger than that in the membrane phase, solute concentration in the two compartments can be related to each other by considering a mass balance equation:

$$C_I = C_I^0 - C_{II} \frac{V_{II}}{V_I} \qquad (7.4)$$

Combining the Eqs. 7.1, 7.2, and 7.4 for the case of a dialysis cell that contains two compartments of equal volume (V_I=V_{II}), we can obtain:

$$\frac{\partial C_{II}}{\partial t} = \frac{D \cdot A \cdot S}{\Delta x V_{II}} (C_I^0 - 2C_{II}) \tag{7.5}$$

where Δx is the membrane thickness. Integrating Eq. 7.5, we obtain the concentration of solute in the diluted compartment as a function of time:

$$C_{II} = \frac{C_I^0}{2} \cdot \left[1 - \exp\left(-2D \frac{AS}{\Delta x V_{II}} t \right) \right] \tag{7.6}$$

Similar expression of solute concentration in the concentrated compartment can also obtained by substituting Eq. 7.6 into Eq. 7.4. Rearrange Eq. 7.6, we have:

$$\ln\left(1 - \frac{2C_{II}}{C_I^0} \right) = -2D \cdot \frac{AS}{\Delta x V_{II}} \cdot t \tag{7.7}$$

When solute adsorbs to the membrane to a significant extent, Fick's second law of diffusion can be used to account for a non-stationary concentration of the solute in the membrane phase. Although the solution for a non-stationary problem based on the Fick's second law of diffusion is readily available in texts dealing with the mathematics of diffusion such as Crank [238], the application of such a solution in practice would require a cumbersome numerical procedure [239]. In this study, to account for the adsorption of solute to the membrane, an approximation has been made to replace C^0_I with real time solute concentration of the concentrated compartment (C_{It}). Eq. 7.7 can be rewritten as:

$$\ln\left(1 - \frac{2C_{II}}{C_{It}} \right) = -2D \cdot \frac{AS}{\Delta x V_{II}} \cdot t \tag{7.8}$$

If the membrane thickness (Δx), membrane area (A), partition coefficient (S), and volume of the dialysis cell are known, Eq. 7.8 can be used to determine the diffusion coefficient based on any given sets of experimental data.

3. *Materials & Methods*

3.1 Representative membranes

Three NF membranes, denoted NF-270, NF-90 (FilmTec Corp., Minneapolis, MN), and TFC-SR2 (Koch Membrane System, San Diego, CA) were used in this study. All of these membranes are made of a thin layer of fully aromatic polyamide on a more porous polysulphone support. Their characteristics have been previously described in detail in Chapter 3.

3.2 Trace contaminants

Radiolabelled estrone-2,4,6,7-3H-(N) was purchased from Sigma-Aldrich (Saint Louis, MO). Once again, physicochemical properties and other characteristics of this compound have been described in Chapter 3. The analytical technique for this compound can also be found in Chapter 3.

3.3 Membrane thickness

Most nanofiltration (NF) and reverse osmosis (RO) membranes consist of a very thin active layer and a supporting layer. The former provides selective transport properties to the membrane while the latter provides mechanical support to the active layer. Adsorption of trace contaminants can induce diffusion across the membrane active layer thickness, which is commonly in the order of a few hundred nanometers or less. Subsequently, such diffusion may reduce the membrane selectivity (see Chapter 4). However, the exact thickness of the active layer is rarely available due to difficulty in determining layer thickness experimentally. The first active layer thickness measurement technique was recently reported by Freger *et al.* [145]. It involves staining the membrane sample with uranium nitrate or sodium tungstate and the use of a Transmission Electron Microscope (TEM). As the polysulfone supporting layer of the membrane is stained with the heavy atoms of uranium or tungsten, while the polyamide active layer is not, TEM image can subsequently reveal the thickness of the active layer. With this technique, Freger *et al.* reported a thickness of approximately 15 nm for the NF-270 membrane [145]. Nevertheless, the procedure is complicated. Furthermore, in some cases, particularly when the supporting and the active layer are interwoven into each other, insufficient resolution may occur and render the accuracy of this technique inadequate. Part of this study attempts to utilise the capacity of Rutherford Backscattering Spectroscopy (RBS) to characterise the active and supporting layer thickness of the membranes using the Ion Bean Analysis (IBA) available at the Australian Nuclear Science and Technology Organisation (ANSTO).

3.4 Ion Beam Analysis

When a charged particle moving at high speed collides with an atom of a target material, it interacts with the electrons and nuclei of that atom. As the result the ion slows down and possibly deviates from its initial trajectory. Also, the target atom may leave its equilibrium position, or it may even be scattered and leave the target. The interaction of ions with target atoms can also lead to the emission of particles or radiation whose energy is characteristic for the particular target atom. In principle, Ion Beam Analysis (IBA) techniques utilise the interaction between the ions and the target atoms,

and can quantify the elemental composition of the target material, determining the thickness of various layers of the target, and measuring the depth profiling of elements in the target.

In this study, the RBS technique was used, with a He^{+1} ion beam, obtained on a HVEE 3MV Tandem accelerator. The energy of the He^{+1} projectiles was 2 MeV. The energy of the scattered He atoms was measured at an angle of 170^{o} using a Si-barrier detector. The signal was then amplified and scanned in energy (Pulse Height Analysis) with a multi channel analyser. The RBS spectra obtained from the signal of sulphur was used to estimate the active and supporting layer thickness.

3.5 Dialysis cell & Experimental protocol

The dialysis apparatus used in this study is shown in Figure 7.2. It consists of two compartments of equal volume, which are separated by the test membrane. An O-ring of 35 mm in diameter is located in between these two compartments and seals them against the membrane to avoid any leakage. Aluminium foil was used to cover these compartments to avoid evaporation. At the beginning of each experiment, one compartment was filled with 70 mL of estrone solution with a concentration of 1000 ng/L and the other was filled with 70 mL of deionised water. The membrane active layer was position to face the concentrated compartment. One mL of sample was taken from each compartment at a specific interval for analysis. Experiments were conducted at a room temperature of 25 ^{o}C.

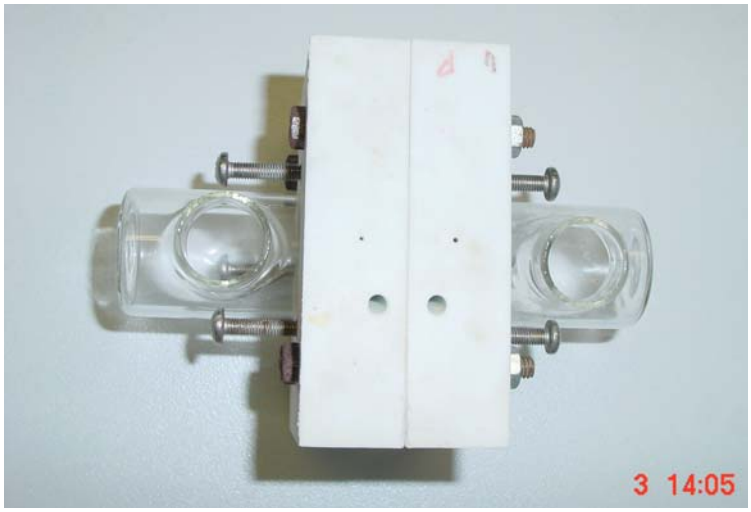


Figure 7.2: The dialysis cell used in this study.

4. *Sorption-diffusion of trace organic NF membranes*

The transport results of estrone in the first 80 hrs in the TFC-SR2, NF-270, and NF-90 membranes are shown in Figure 7.3. It was found that estrone strongly adsorbed (or partitioned) into all three

membranes of in this study. The TFC-SR2 has a very open pore radius of 0.64 nm, that of the NF-270 is 0.42 nm, and the NF-90 is a tight NF membrane with a pore radius of 0.34 nm (see chapter 5).

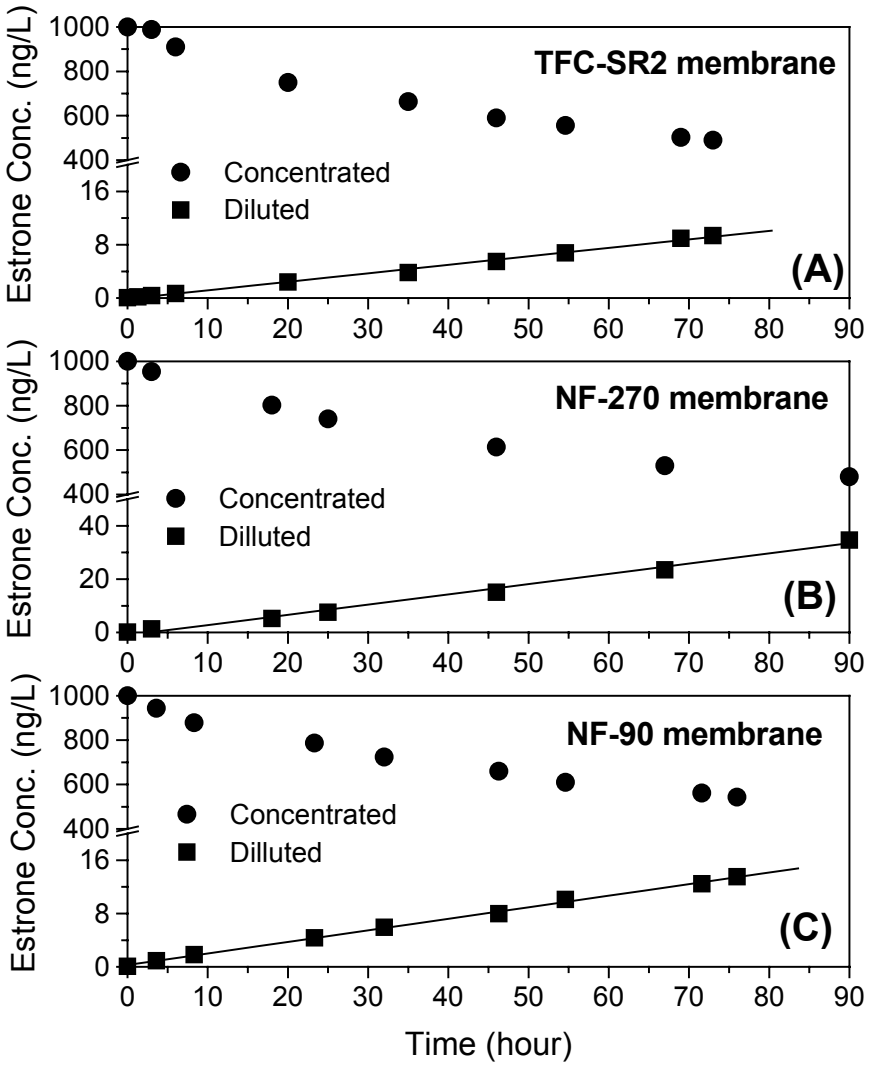


Figure 7.3: Estrone concentration in the concentrated and DI water compartments as a function of time in dialysis experiments with (A) TFC-SR2, (B) NF-270, and (C) NF-90 membranes. Initial estrone concentration was 1000 ng/L (Experimental conditions were as follows: pH=6, temperature=25 ^{o}C.)

It is expected that membranes with a small pore size or low free volume will have more hydraulic resistance (or friction), which hinders the transport of the solute (or penetrant) within its polymeric matrix. However, despite the fact that these membranes are markedly different in the average pore size, the amount adsorbed to the TFC-SR2 membrane appears to be only marginally higher than that of the NF-270 and NF-90 membranes. Without a pressure differential, transport of estrone in the polymeric membrane is purely governed by a concentration gradient and affinity of the solute

toward the membrane polymer. The latter depends on the availability of the adsorptive sites (if hydrogen bonding is responsible for adsorption) or adsorptive surface (if hydrophobic interaction is responsible for adsorption) of the polymeric membrane. Although these three membranes are made of similar polymers (polyamide on polysulfone support), the presence of additives, other co-monomers, and surface modification agents during the manufacturing process may render a distinctive comparison between them, particularly between membranes from different manufacturers. In addition, both hydrogen bonding and hydrophobic interaction are likely to play a role; it is conceivable that further studies where the same polymer of different thickness is investigated may reveal more clear findings.

As can be seen in Figure 7.3, there is a low but apparent flux of estrone across the membranes reflected by a small increase in estrone concentration in the DI water compartment. It is noteworthy that the NF-90 membrane has an average pore size of 0.34 nm, which is significantly smaller than the equivalent Stokes radius of an estrone molecule (approx. 0.42 nm). Estrone diffuses across the membrane and estrone concentration in the other compartment appears to increase linearly as a function of time. Remarkably, the observed transport profile is quite similar to that of supported membranes used for selective transport of certain metal ions [241]. In the absence of any applied pressure, the flux of estrone across the polymeric membrane is low. However, it is anticipated that with a transmembrane pressure across the membrane, the diffusion process may be enhanced considerably, which would possibly contribute to a lower retention than expected by a steric hindrance mechanism.

Results reported here appear to contradict an intuitive view that the membrane is an "absolute physical" barrier, which would retain solutes larger than its pore. This is because, in the past, primary solutes of concern were mostly particulate matter, bulky macro-organics, or dissolved salts, which are relatively chemically inert to the membranes, except perhaps the filtration of dissolved salts by ion exchange membranes. While studies investigating the sorption and diffusion of small organics in polymeric membranes remain scattered in the literature [131, 239, 240, 242], there are several rich and comprehensive reviews relating to such phenomena in the biomedical discipline, mostly addressing specific transport of certain penetrants in biological membranes [243, 244]. In regard to certain small organics, perhaps it is more appropriate to define a polymeric membrane as a physicochemical barrier, where solute affinity toward the membrane may play an important role in the transport phenomena [116].

5. *Membrane thickness characterisation*

According to the manufacturers, the membranes are made of a thin layer of polyamide cast on a layer of microporous polysulfone. The former is responsible for separation, while the latter provides mechanical support to the membrane. Average pore radius of the latter is in the order of 0.1 μm or more, and this microporous layer does not contribute to the separation process or the membrane hydraulic resistance. As can be seen from the polymeric structures of the polyamide and polysulfone layer (see Figure 7.4), nitrogen and sulfur can be used as a signatory element for each of them. Nitrogen is only present in the active layer while sulfur is only present in the supporting layer.

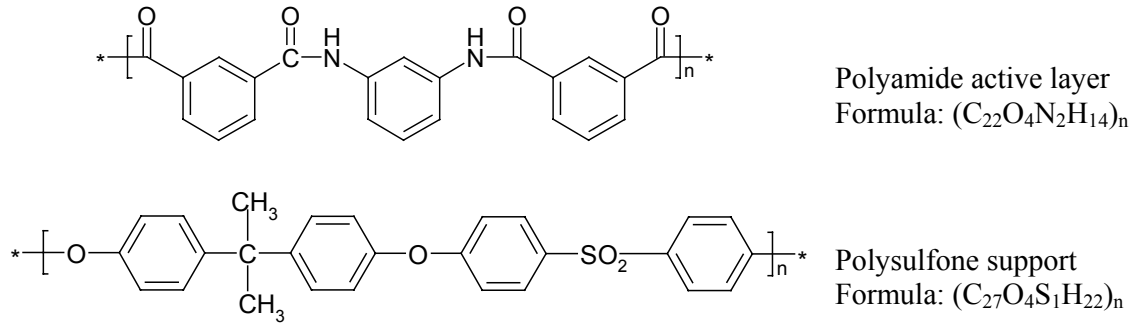


Figure 7.4: Chemical structure of the polyamide active layer (top) and the polysulfone supporting layer (bottom). Note that proprietary chemical modifications may vary this.

RBS spectrum of sulfur obtained from the TFC-SR2, NF-270, and NF-90 membranes are shown in Figure 7.5, Figure 7.6, and Figure 7.7, respectively. As sulfur is only present in the supporting layer, it must pass through the supporting layer and then the active layer before reaching the detector. SIMNRA (version 5.0) software was used to examine the RBS spectra to determine the thin film unit (TFU) density of sulfur for each membrane. The thickness of both the active layer and the supporting layer were subsequently determined corresponding to these TFU density values. The results are presented in Table 7.1.

It is notable that values reported in Table 7.1 are comparable to the active layer thickness of NF membranes reported elsewhere [131, 144, 145]. The active layers of the selected membranes are approximately in order of 3 magnitudes smaller than the supporting layers. However, as discussed previously the supporting layer of these membranes is microporous with average pore size up to several micrometers [131], it is not expected to contribute to the separation as well as hydraulic resistance of the membranes. The NF-90 membrane has a considerably thicker active layer compared to the NF-270 and TFC-SR2 membranes but lower than that of typical RO membranes

which usually have an active layer thickness of more than 300 nm [131]. In fact, the NF-90 can be classified as a low pressure RO membrane.

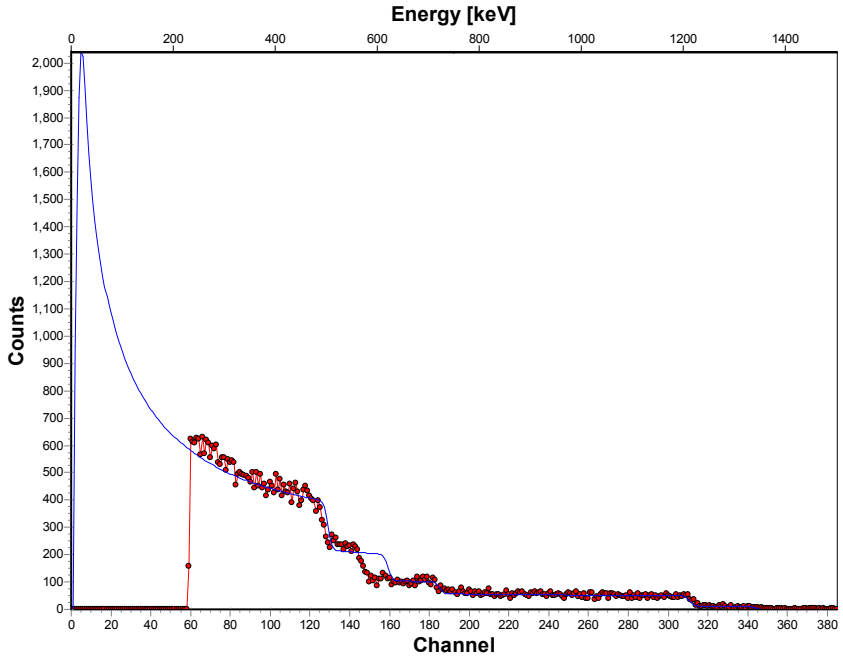


Figure 7.5: RBS spectra of sulphur in the TFC-SR2 membrane and the simulated spectra obtained with the SIMNRA software (version 5.0). Experimental conditions: beam of He^{+1} ions of 2 MeV in energy and the energy of the recoiled atoms was measured at an angle of 170° using a Si-barrier detector.

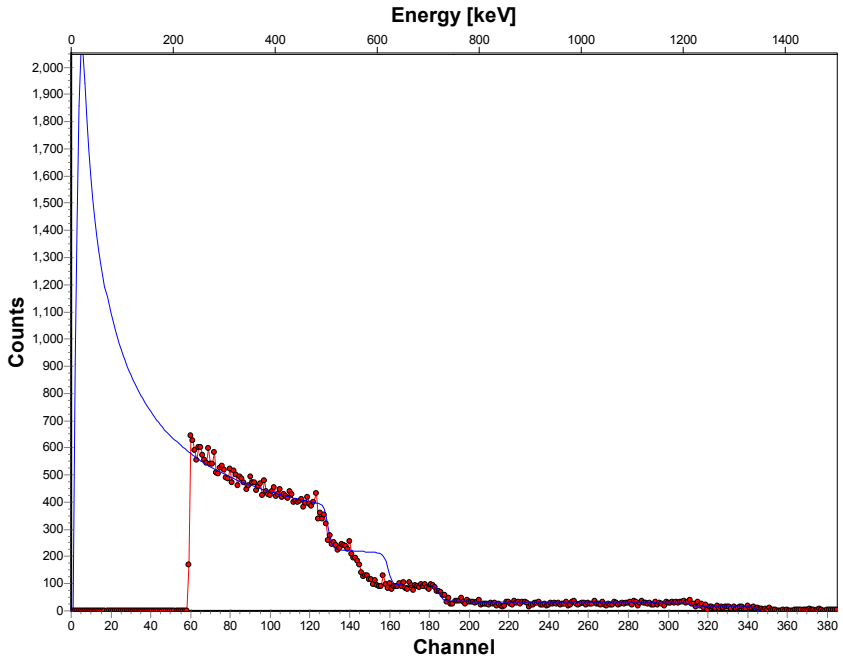


Figure 7.6: RBS spectra of sulphur in the NF-270 membrane and the simulated spectra obtained with the SIMNRA software (version 5.0). Experimental conditions: beam of He^{+1} ions of 2 MeV in energy and the energy of the recoiled atoms was measured at an angle of 170° using a Si-barrier detector.

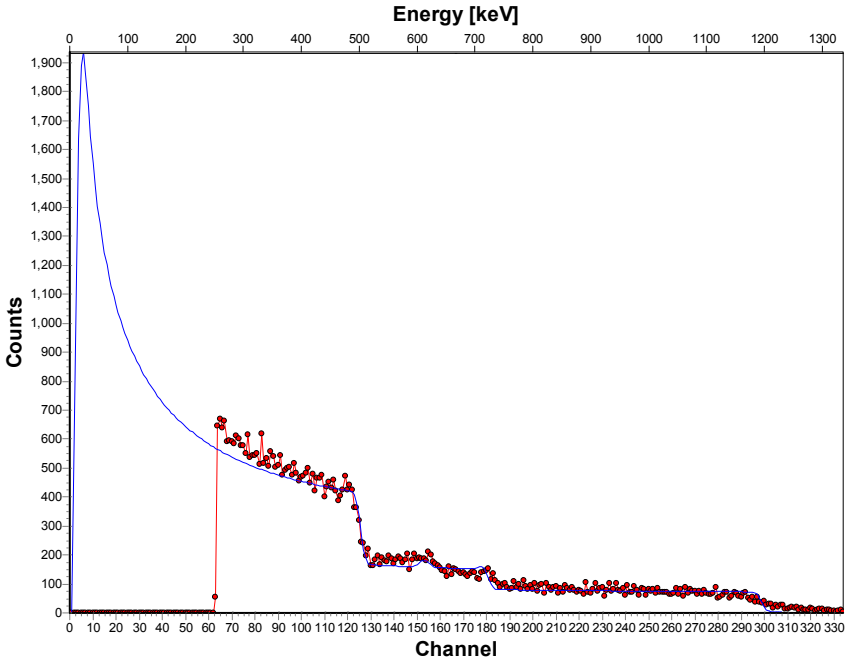


Figure 7.7: RBS spectra of sulphur in the NF-90 membrane and the simulated spectra obtained with the SIMNRA software (version 5.0). Experimental conditions: beam of He^{+1} ions of 2 MeV in energy and the energy of the recoiled atoms was measured at an angle of 170° using a Si-barrier detector.

Table 7.1: Thickness of the active and supporting layers of the NF-270, TFC-SR2, and NF-90 membranes. Values of the active layers are in a range corresponding to the range of the Thin Film Unit (TFU) density of the membrane polymer.

	NF-270		NF-90		TFC-SR2	
	TFU density (at/cm^2)	Thickness (nm)	TFU density (at/cm^2)	Thickness (nm)	TFU density (at/cm^2)	Thickness (nm)
Active layer	$5 \cdot 10^{15}$	27	$5 \cdot 10^{15}$	134	$5 \cdot 10^{15}$	27
	$15 \cdot 10^{15}$	80	$20 \cdot 10^{15}$	214	$20 \cdot 10^{15}$	107
Supporting layer	$2.4 \cdot 10^{21}$	$134 \cdot 10^{3}$	$2.4 \cdot 10^{21}$	$193 \cdot 10^{3}$	$2.4 \cdot 10^{21}$	$161 \cdot 10^{3}$

The membrane active layer thickness was reported in a range rather than an absolute value. For example, the active layer thickness of the NF-270 membrane is in between 27 to 80 nm (Table 7.1). This is because the integration between the active and the supporting layers causes an unclear and undistinguished the boundary between these two polymer phases. As previously reported by Freger and co-workers [144, 145], their technique to characterise the membrane active layer may also be subjected to similar problem of low resolution due to the infusion between the polyamide and polysulfone phases.

6. *Diffusion coefficients of estrone in polymeric membranes*

The partitioning coefficient of estrone between polyamide polymer and water was determined to be 128 using the non-filtration adsorption isotherm of estrone to the membrane as presented in Chapter 6. Groβ and Heintz studied the diffusion of 7 aromatic compounds in dense polyether-block-polyamide (PEBA) [239]. They reported that for a moderate partitioning coefficient (of less than 300), the difference between stationary and non-stationary models is indistinguishable. Consequently, the approximation in Eq. 7.8 is justified.

Eq. 7.8 was used to determine the extent of diffusion of estrone in the three membranes by plotting $Dt/\Delta x$ against dialysis time. As mentioned above, the partitioning coefficient was 128. Volume of the dialysis compartment was 70 mL and effective membrane area was 9.6 cm^2. As can be seen in Figure 7.8, the ratio of the diffusion coefficient over the membrane thickness ($D/\Delta x$) can be obtained by taking the slope of a linear fitted line. $D/\Delta x$ depends only on the membrane polymeric material and its morphology. $D/\Delta x$ of the NF-270 membrane is higher than that of the NF-90 membrane because it has a larger pore size and hence results in less friction to the diffusion of estrone across the membrane. However, it is surprising to note that the very loose TFC-SR2 has a quite similar $D/\Delta x$ value to that of the tight NF-90 membrane. This is in contradictory to the observed pore size difference between the two membranes, and perhaps can only be explained by the difference in surface roughness of the membranes and to some extent the difference in composition of the polymeric material due to proprietary chemical modification.

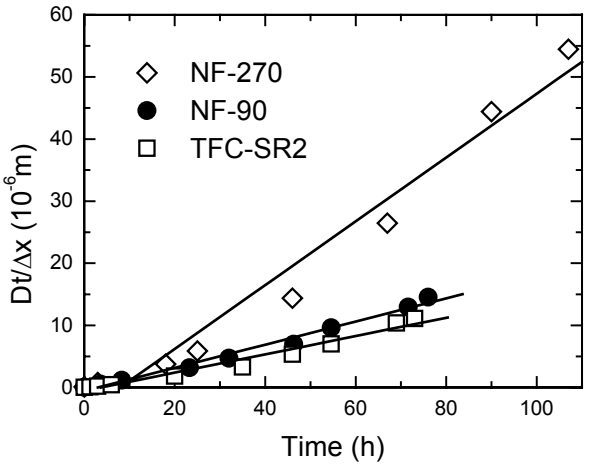


Figure 7.8: $Dt/\Delta x$ as a function of dialysis time for the TFC-SR2, NF-270, and NF-90 membranes.

The diffusion coefficients of estrone in three membranes in their active layer are calculated based on the thickness of the active layers as measured above, and are presented in Table 7.2. These values correspond to the minimum and maximum active layer thickness. The active layer of these membranes is made of a similar type of polymer. Despite their difference in the free volume, which is reflected by the difference in their average pore size, the diffusion coefficients of estrone are quite similar, varying in a small range between 37 to 377 (10^{-16} m^2s^{-1}).

Table 7.2: Diffusion coefficients D of estrone in three membranes selected in this investigation.

Membrane	Active layer thickness (nm)	D (10^{-16} m^2s^{-1})
TFC-SR2	27 – 107	37 - 147
NF-270	27 – 80	124 - 368
NF-90	134 –214	236 – 377

Values reported here are comparable to the diffusion coefficient of small molecular weight drugs in high density polyethylene and polystyrene as documented by Smith and Lonsdale [245]. These are approximately 5 orders of magnitude smaller than the diffusion coefficient of estrone in an aqueous solution. However, given that the active layer thickness of the membrane is extremely thin, transport as a result of such small diffusion coefficients can be quite considerable. Furthermore, these values only present the diffusion coefficient of estrone in a static system. It is possible that a transmembrane pressure can significantly influence the diffusion processes.

It is interesting that the diffusion coefficient of estrone in the TFC-SR2 membrane that has the most open pore size is lowest amongst the three selected membranes. In addition, estrone diffusion coefficients in the NF-270 and NF-90 membranes are quite comparable despite of their difference in average pore size. Both of these membranes are from the same manufacturer. It is noted that the NF-270 membrane has a piperazine based polyamide active layer [144] while the NF-90 membrane is a typical fully aromatic polyamide thin film composite membrane. Consequently, the NF-270 membrane has a smoother surface than that of the NF-90 membrane. It is speculated that the actual polymer composition can be also an important factor determining the diffusion coefficients of trace organic contaminants such as estrone in the membrane active layer.

7. *Diffusion mechanisms in polymeric membranes*

A number of studies have been devoted to understand the diffusion of hormones in polymeric membranes [143, 219, 246-248] mostly for drug delivery purposes. The active skin layer of the TFC-SR2, NF-270, and NF-90 membranes is made of aromatic polyamide, which is a hydrophobic material. However, water is sparsely soluble in this polymer and the diffusion process of natural

hormones in the membrane takes place in a polymeric matrix saturated with small amounts of water. Although viscous flow does not contribute to the transport of natural hormones across the membrane, the presence of water is thought to play an important role in facilitating the diffusion process. Diffusion of hormones in a dense polymeric phase is accomplished by a series of successive jumps from one equilibrium position to another, which usually involves the formation and breaking of secondary bonds. Such "make-and-break" action can be the result of switching between two bonding sites or between a hydrophobic bond to a substrate and a hydrogen bond to water [142, 143]. Given a moderate to high log K_{ow} (or hydrophobicity) of estrone as well as other steroid hormones and hormonal mimicking compounds (see Chapter 3 for detail), hydrophobic interaction between such solutes and hydrophobic parts of the membrane polymer is most likely. Simultaneously, there is an abundant number of studies, mostly in biomedical science, confirming the role of specific hydrogen bonding in the binding of steroid hormones to their receptors and other various substrates [221, 244, 249, 250]. The membrane polymer may not be as homogeneous and specific as a biological membrane or a hormonal receptor. Although there is insufficient information at this stage to conclusively examine the mechanisms, it is likely that both hydrophobic interaction and hydrogen bonding are simultaneously governing the interaction between polymeric membranes and steroid hormones or hormone mimicking compounds.

Both hydrophobic and hydrogen bonds have energies in the order of a few kJ/mol. In comparison, at room temperature the kinetic energy amounts to 2.5 kJ/mol, which means that such individual bonds can "make-and-break" quite readily [142]. Several researchers have demonstrated that such a process is temperature sensitive and membrane permeation depends strongly on temperature in the range of 10 to 50 ^{o}C [143, 246, 247]. This subsequently gives rise to a "random walk" movement of adsorptive organic solutes, which is a precursor for the sorption diffusion process under a chemical potential gradient.

8. *Conclusions*

Results presented in this chapter provide clear evidence of a small but apparent diffusion flux of estrone in the polymeric membranes despite the fact that the molecular size of estrone was larger than the membrane pore. It is expected that with a transmembrane pressure across the membrane, this diffusion can be enhanced. To further elucidate the significance of the diffusion process in the nanofiltration of trace organic contaminants, the Rutherford Backscattering Spectroscopy technique was employed to measure the thickness of the membrane active and supporting layers. The diffusion coefficients of estrone in the polyamide active layers of the three selected membranes

were then determined. The diffusion coefficients of estrone in the active layers of these membranes were quite low. However, because their active layers were also very thin, the separation efficiency of certain trace organic contaminants could be strongly influenced by diffusion. Diffusion was thought to be accomplished via the formation and breaking of secondary bonds such as hydrogen and hydrophobic bonding.

Chapter 8

Complexity of real applications

1. *Introduction*

Operating condition is essential in maintaining the performance of any membrane filtration process in both contaminant removal efficiency and water production. Variation in operating condition may have considerable effects on the membrane performance and to date this particular issue has attracted many dedicated investigations. Such great efforts have resulted in several benchmark parameters or rule of thumbs, which are widely used in the membrane industry. One of the most well known examples is perhaps the critical flux concept [251-253]. In fact, membrane manufacturers typically associate their product warrantee within a range of several operating parameters such as feed flow rate, pressure, permeate flux, and recovery. However, these rule of thumbs remain vague and broadly conservative. In contrast to hydraulic operating condition, which can be relatively stable, it is not possible to maintain a constant feed water matrix and its particulate content. Zhang et al. [254] reported clear effects of solution matrix on pesticide retention when they examined atrazine and simazine retention in distilled, tap, and river water matrices, although the precise underlying mechanisms remain unclear.

Of a particular note is the dearth of information on the effects of operating conditions (such as transmembrane pressure and cross flow velocity) and feed water matrix on trace contaminant retention. Most findings available to date are sometimes contradictory with one another, probably indicating that effects of operating condition and solution chemistry on membrane performance are often contaminant specific. For example, it was reported that an increase in applied pressure would increase fluoride retention by a nanofiltration membrane [255], whereas no apparent pressure effects on arsenic retention was reported in another study [256]. In contrast, several other researchers reported an opposite observation in the nanofiltration process of some trace organics where retention decreased as applied pressure increased [45, 116, 136]. While pesticide retention was reported to be enhanced by the presence of organic matter in the feed solution by several researchers [66, 67, 257], such phenomenon was absent in a study by Berg *et al.* [65]. This is

probably attributable to the heterogenic nature of various constituents in the aqueous solution and the diversity of physicochemical properties of trace contaminants.

Similar to many other dissertations, this study as a whole attempted to reveal fundamental findings and the underlying mechanisms in which trace contaminants were removed or transported within the membranes. Experiments in previous chapters were conducted in a clean water matrix under stable operating conditions. It was not the aim of this dissertation to directly translate all of such fundamental findings to a real membrane filtration application as such. However, given a severe lack (indeed the unavailability) of information from full scale applications in regard to the removal of steroid hormones, hormone mimicking compounds and pharmaceuticals by membrane filtration, it is essential to be able to use the results reported here for estimation purposes.

This chapter relates the results of Chapters 4 to 7 to real life applications of NF/RO membrane filtration processes, where trace contaminants such as hormones and pharmaceuticals are of particular concern. Operating condition effects - namely cross flow velocity and applied pressure – on retention of the steroid hormone estrone were investigated. This chapter also examined the influence of feed water composition on trace organic retention by using humid acids, cellulose particles, and a surfactant (sodium dodecyl sulfate) as model constituents. Interactions between the steroid hormone estrone and such constituents were related to both adsorption and retention and were discussed in detail.

2. *Materials & Methods*

2.1 Representative membranes

Four commercial membranes were selected for investigation in this chapter, the TFC-S, TFC-SR2 supplied by Koch Membrane Systems (San Diego, USA), X-20 and XN-40 supplied by Trisep Corporation (Goleta, USA). Their characteristics have been described in detail in Chapter 3.

2.2 Trace contaminants & reagents

Radiolabelled estrone-2,4,6,7-^{3}H-(N) (92 % purity) was purchased from Sigma Aldrich (Saint Louis, MO). Secondary effluent was obtained from the Brendale wastewater treatment plant in Queensland, Australia. Previous analysis showed that it contains about 10 mg/L total organic carbon (TOC), 50 mg/L of sodium and 10 mg/L of calcium [174]. Natural organic matter (NOM) was concentrated from Mooney-Mooney dam in a previous project [16]. Surface water was synthesized using 10 mg/L of NOM in background electrolyte (20 mM NaCl and 1 mM $NaHCO_3$).

Cellulose, technical humic acids, and analytical grade sodium dodecyl sulfate (SDS) were purchased from Sigma Aldrich (Saint Louis, MO) to represent likely constituents that may present in wastewater. All other chemicals were of analytical grade, unless otherwise stated.

2.3 Filtration systems & experimental protocol

As previously mentioned, this chapter aims to investigate the operational effects and effects of various constituents that may be present in feed water on retention of trace organics during membrane filtration processes. The former was studied using a cross flow filtration system, which would allow a replicate condition as in a real application, while the latter was studied using a dead end stirred cell to ensure reproducibility and experimental control.

The dead end filtration system has been previously described in Chapter 3. A series of 5 identical estrone solutions (100 ng/L) were consecutively filtered through a single membrane sample to achieve an equilibrium state between the steroid hormone estrone and the membrane. A permeate volume of 120 mL was collected in each filtration cycle. The remaining feed solution (retentate) was also collected for analysis and the stirred cell was filled with a fresh estrone solution for the next filtration cycle. The applied pressure was 5 bar.

The ANSTO cross flow filtration test unit was used in this chapter. Details about this filtration test unit can also be found in Chapter 3.

3. *Retention in real water matrix*

Organic compounds occur naturally and are ubiquitous in any aquatic environment where they often determine the surface properties of any solids in contact with water. Organic matter found in water spans a wide spectrum, with molecular weights ranging from less than a hundred to several hundred thousands Daltons (grams per mol). While natural water contains compounds mostly on the lower end of this spectrum, secondary effluent contains even lower molecular weight organics as they have generally been broken down during biological treatment processes. Although bulk organics are not considered harmful to human health, they are relevant precursors for the formation of carcinogenic trihalomethanes (THMs) and other disinfection by-products after disinfection. Further, as contaminants like estrone can bind to organic matter, their presence can enhance retention and generally determine the fate of compounds. Finally, a fraction of organic matter may compete with estrone for adsorptive sites. Consequently, this competition can also affect retention where adsorption is a dominant factor.

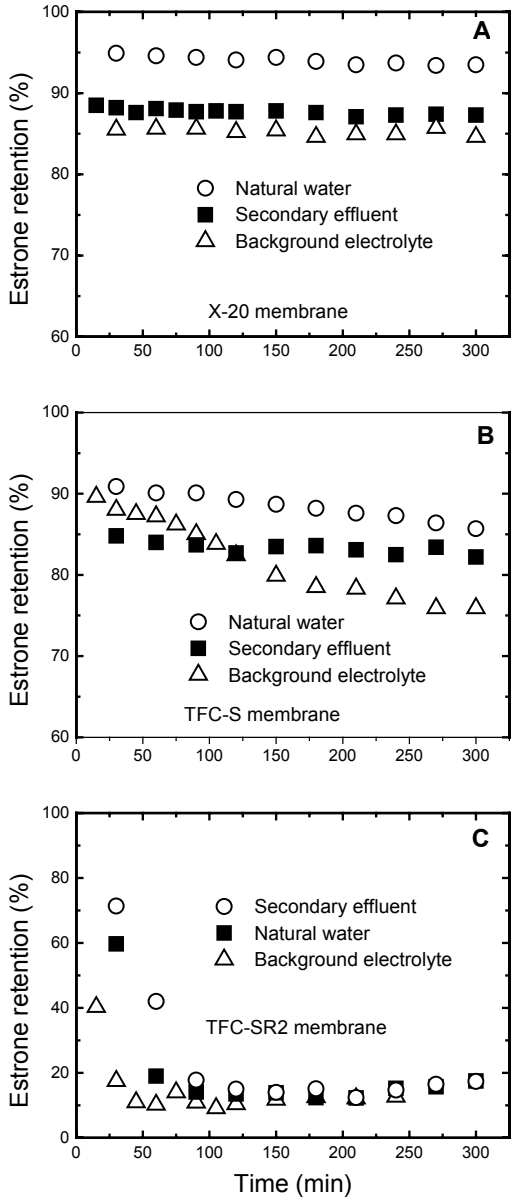


Figure 8.1: Estrone retention in different matrix solution by X-20 (A), TFC-S (B) and TFC-SR2 (C) (10 bar, cross flow velocity of 0.073 m/s, pH 8, surface water and secondary effluent solutions contain 10 mg/L organic matter).

To study the effects of organic matter on estrone retention, experiments were conducted in three different matrix solutions: pure background electrolyte matrix, secondary effluent, and synthetic surface water (natural organic matter concentrated from Mooney Mooney Dam in background electrolyte). Ionic strengths of the clean matrix and the synthetic surface water were prepared to be

approximately that of secondary effluent. Likewise, the organic content of synthetic surface water was selected to be identical to that of secondary effluent (TOC = 10 mg/L).

Estrone retentions in the different matrix solutions by X-20, TFC-S and TFC-SR2 membranes are shown in Figure 8.1A, B, and C, respectively, whereas TOC retention in secondary effluent is shown in Figure 8.2. It appears that estrone retention is enhanced by the presence of organic matter. Furthermore, this enhancement seems to be stronger for natural water than in secondary effluent (containing organic matter of smaller molecular weights). Large molecules can be retained more effectively, hence, exert a stronger influence on estrone retention. However, this phenomenon is not observed for TFC-SR2 membranes, possibly due to its larger pore size. Reported results are consistent with several earlier studies [66, 67, 257]. Agbekodo *et al.* [67] investigated the influence of natural organic matter concentration on atrazine and simazine retention by the NF-70 membrane and a clear increase in atrazine and simazine retention as a function of organic matter concentration in the feed solution was reported.

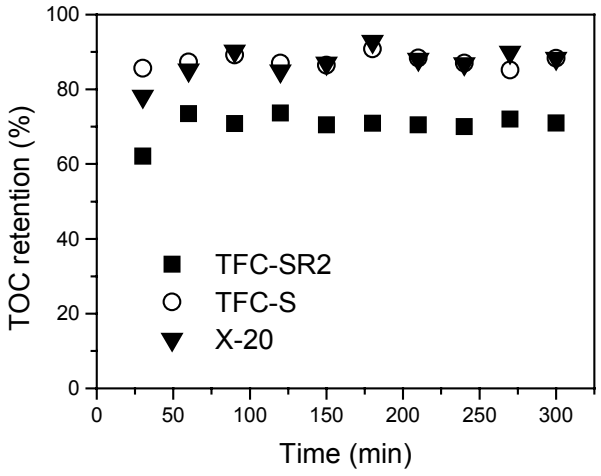


Figure 8.2: TOC retention (secondary effluent, P=10 bar, cross flow velocity of 0.073 m/s, pH 8).

4. *Effects of cross flow velocity & pressure on trace organic retention*

Understanding the impact of operating variables on retention of trace contaminants is of paramount importance from design as well as operational points of view. The influence of cross-flow velocity and operating pressure on estrone retention was examined in this study. The XN-40 membrane was selected as a result of a previous study [94] as it exhibits medium range estrone retention. To eliminate the influence of adsorption, the membrane was equilibrated with estrone solution in background electrolyte matrix for 5 hours at 10 bar. Cross-flow velocity was then varied from 0.073 m/s to 0.24 m/s. A fresh solution was used to examine the operating pressure effects on retention.

After equilibrating the membrane with the same procedure, the pressure was varied from 10 to 25 bar. Three samples at each cross-flow velocity or operating pressure were taken for analysis at an interval of 15 minutes.

Estrone retention as a function of cross-flow velocity is shown in Figure 8.3. An increase in cross-flow velocity can reduce the polarization concentration at the membrane-bulk solution interface. The effect could lead to an increase in retention. However, no effects of cross-flow velocity on estrone retention were observed in this study. As estrone adsorbs onto the membrane surface, the estrone concentration within the membrane can be higher than that of the polarization layer. Within the limited range of cross flow velocity investigated here the polarization concentration effect appears to be negligible.

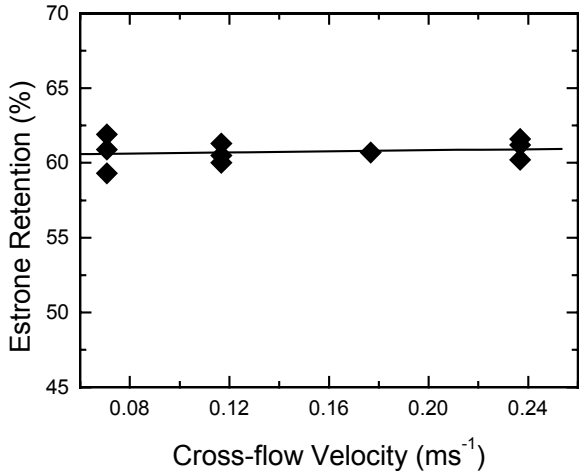


Figure 8.3: Estrone retention as a function of cross flow velocity (XN-40 membrane, 1 mM $NaHCO_3$, 20 mM NaCl, pH 8).

The results are different for a variation in operating pressure. Figure 8.4 shows that estrone retention decreases by 15% as the pressure increases from 10 to 25 bar. In general, ignoring the concentration polarization effect, solute retention increases with pressure up to an asymptotic value. However, for organic solutes that have strong interaction with membrane polymers, retention may decrease with pressure [258]. It has been reported that retentions of chlorophenol [116], chloroform [45], and nonyl phenol [136] decrease as pressure increases. Interestingly, these contaminants were similarly reported to be able to adsorb to the membrane. While the results are consistent, a plausible explanation is to date not available and it is hypothesised that pressure influences the membrane-solute interactions.

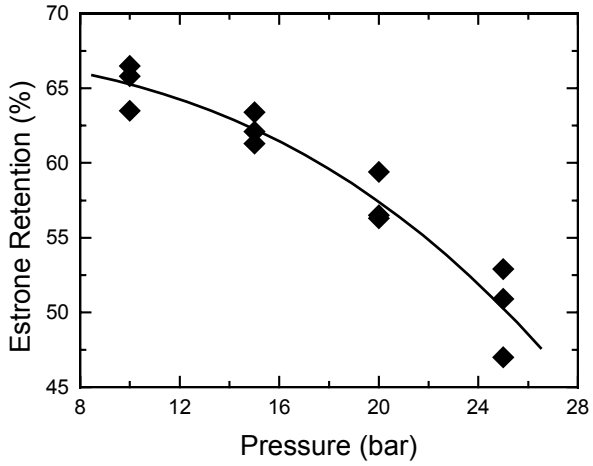


Figure 8.4: Estrone retention as a function of operating pressure (XN-40 membrane, 1 mM $NaHCO_3$, 20 mM NaCl, cross flow velocity of 0.073 m/s, pH 8).

Solute membrane interactions can be dictated by friction (governed by hydrodynamic conditions) and diffusion (governed by chemical concentration gradient). The average pore diameter of the XN-40 membrane was estimated to be in the same order of magnitude as the molecular size of estrone, such interactions can be critical. An increase in pressure results in an increase in permeate flux; and hence the drag force within the membrane pores also increases. Consequently, desorption of estrone can be enhanced or time for adsorption reduced due to the lower residence time in the membrane which may contribute to the drop in retention. In addition, an increase in pressure will also lead to an increase in permeate recovery and ultimately an increase in concentration polarization, which further reduces the retention.

5. *Interaction with various constituents in the solution matrix*

In secondary treated effluent and almost any natural water bodies, constituents such as organic/inorganic particles and organic matter are ubiquitous, although their concentration can vary markedly. Surfactants originating from laundry, shampoo, and other personal care products are also likely to present in wastewater to some extent. Given the tendency of trace organic contaminants to interact with such constituents, it is important to understand their impacts on the filtration processes.

5.1 Trace organic estrone physicochemical properties

As previously discussed in Chapter 3, estrone has a low solubility in water. It $\log K_{ow}$ value (of 4.54) suggests a hydrophobic nature and moderate to high binding tendency to organic colloids and macromolecules in water. Laboratory studies indicates that hydrophobic organics such as estrone

can adsorb moderately onto sediment [171], activated sludge [259, 260], and particulate matter both organic and inorganic [260]. The acid dissociation constants, pK_a, of estrone is 10.4 [124]. On the other hand, it is most likely that the hydroxyl functional group of estrone can facilitate the formation of hydrogen bonding between the molecule and functional moieties of the membrane surface. Theoretically, estrone can be either a proton-donor or a proton-acceptor species. Furthermore, it has been widely accepted in the literature that hydrogen bonding is a primary interacting mechanism between steroid hormones such as estrone and estradiol and their receptors or biological membranes [221, 224, 244, 249, 250]. Molecular structure of estrone has been shown previously in Chapter 3.

5.2 Physicochemical properties of cellulose, SDS, and HAs

Cellulose is an insoluble polysaccharide that consists of few hundreds up to few thousands of β-glucose units. Although cellulose molecules contain a large number of hydroxyl functional groups, such functional moieties are readily occupied by intra and inter hydrogen-bonding formation between cellulose molecules themselves (see Figure 8.5). In addition, cellulose molecules are often large and bulky. As a combination effect, cellulose is relatively inert to chemical interactions.

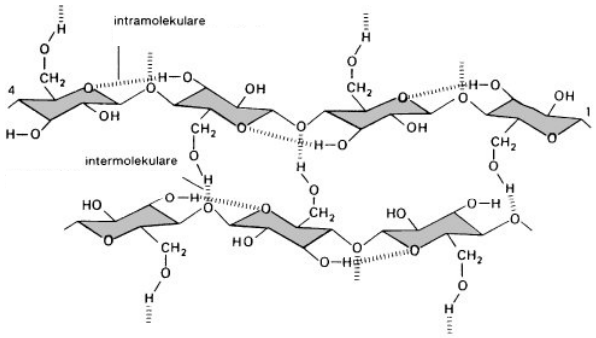


Figure 8.5: Representative molecular structure of cellulose [261].

Size characterisation measurements indicate that the cellulose particles used in this chapter are much more larger than the membrane pore. The D_{10} value of cellulose (presents the diameter at which 10 % of the particulate matter diameter is smaller than this value) is 2.95 μm [262]. In comparison, the TFC-SR2 membrane pore radius is approximately 0.64 nm (see Chapter 4). In fact, complete (100%) cellulose retention was observed with all experiments using the TFC-SR2 membrane (measured by turbidity, data not shown). This implies that the cake layer formed by the accumulation of particulate matter on the membrane surface can be very porous and may not result in measurable fouling if no other constituents are present. Consequently, the influence of cellulose on estrone retention would be largely governed by estrone – cellulose interaction or in other words the partition of estrone to cellulose particles.

On the other hand, surfactant is thought to be quite reactive. Sodium docecyl sulfate ($CH_3(CH_2)_{11}OSOO_3Na$) is an anionic surfactant that by definition consists of a hydrophobic tail and an anionic head, giving it the amphiphilic properties required for a surfactant. In other words, a surfactant can interact with a hydrophobic molecule or surface via its tail as well as partition into an aqueous solution due to the presence of its hydrophilic head. Taking advantage of this amphiphilic nature of surfactant, it is often used as a penetrant enhancer [243] or to modify the adsorption and release processes [263] in biomedical science, particularly for drug delivery purposes.

It has been reported that interaction between hydrophobic drugs and surfactant may cause dramatic changes in solubility or in the rheological behaviour of the drugs in the diffusion and penetration processes through skin and mucous membranes [263]. In a membrane filtration system, polymer/surfactant interactions can be governed by (a) hydrophobic interactions between the non-polar surfactant tail and the hydrophobic backbone of the polymer, (b) hydrogen bonds if the membrane has some carboxylic functional groups and surfactant possess some proton donor, or (c) electrostatic interactions between the polar heads of the surfactant and fixed charged groups of the polymers. Similar interactions may also be expected between trace organics and surfactant. Consequently, surfactant may influence the filtration process of trace organic contaminants via solute-solute interaction or via the modification of the membrane surface properties.

5.3 Flux behaviour during dead end filtration tests

The permeate flux profile a typical five-cycle dead end filtration experiment using the TFC-SR2 membrane is showed in Figure 8.6. Because cellulose is completely retained by the membrane, a cake layer of cellulose is formed on the membrane surface. As delineated previously, this cake layer is expected to be quite porous and. Consequently, only a small degree of permeate flux decline was observed after each successive filtration cycle. This is probably because the absence of multivalent cations such as Ca^{2+} which can act as a bridging or complexing agent [264-266], resulting in a denser cake layer and hence more severe flux decline. However, Ca^{2+} was not used in this chapter since the primary objective here is to elucidate the interactions between the trace organic estrone and other constituents in the feed solution. It is also noteworthy that because salt retention of the TFC-SR2 membrane is relatively small, the osmotic pressure due to concentration polarisation is expected to be negligible.

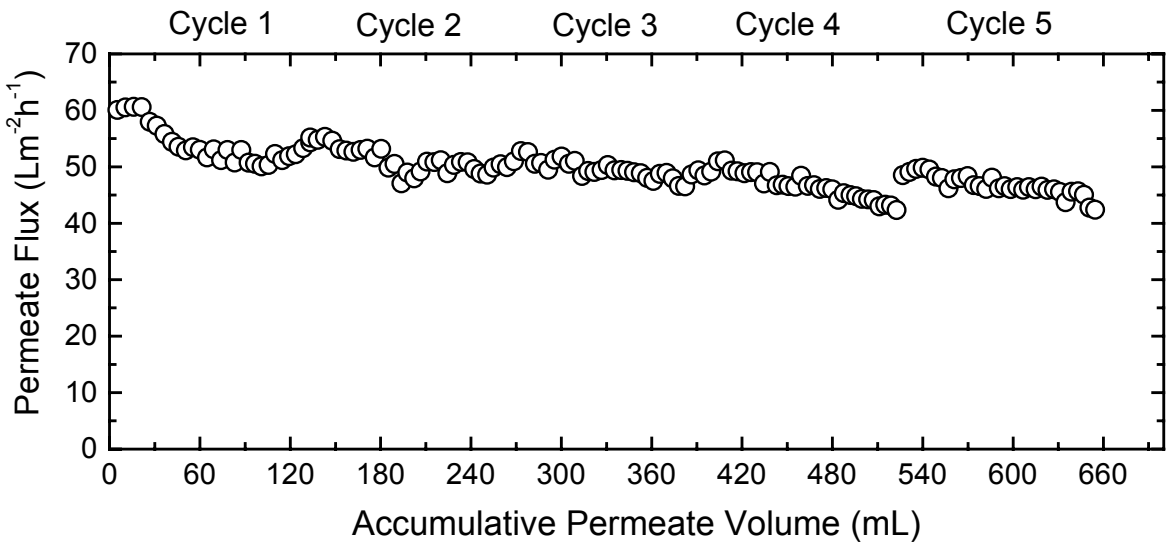


Figure 8.6: Permeate flux profile of a five-cycle dead end stirred cell filtration test using the TFC-SR2 membrane (feed solution contains 100 ng/L estrone, 20 mM NaCl, 1 mM $NaHCO_3$, and 60 mg/L of cellulose; pH ~ 6; and applied pressure of 5 bar).

5.4 Filtration volume effects

Since the average pore radius of the TFC-SR2 membrane is estimated to be 0.64 nm (see Chapter 4), considerably larger than the size of an estrone molecule (Stockes radius of 0.41 nm), the TFC-SR2 membrane is expected to exhibit relatively low estrone retention. However, due to considerable estrone adsorption to the membrane polymer, retention at the initial filtration stage is quite high as removal is predominantly governed by estrone adsorption. This is evident in Figure 8.7 and Figure 8.8, in which estrone retention values as a function of filtration cycles obtained by the stirred cell at pH 6 and 12 are presented, respectively.

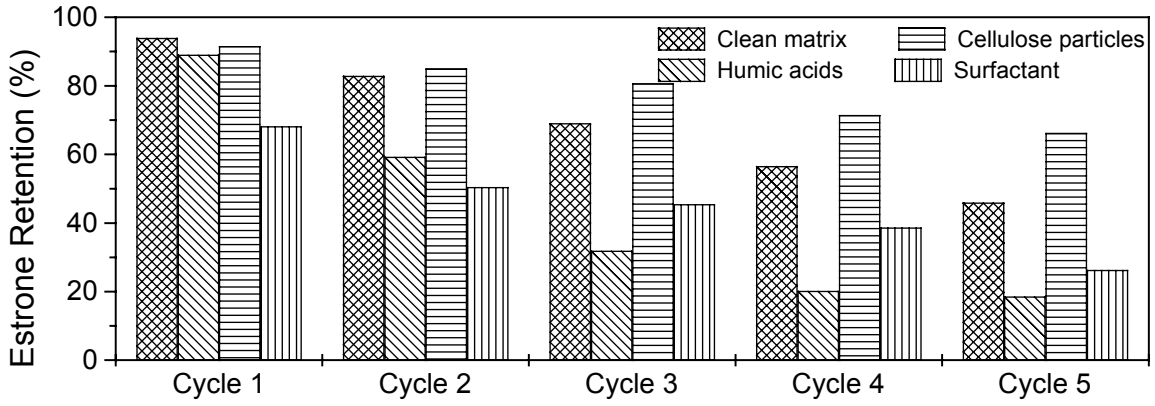


Figure 8.7: Estrone retention by the TFC-SR2 membrane at 5 filtration cycles at pH 6 (Clean background electrolyte contains 100 ng/L estrone, 20 mM NaCl, and 1 mM $NaHCO_3$; humic acid solution contains 20 mg/L of HAs, cellulose solution contains 60 mg/L of cellulose, and surfactant solution contains 1 mM SDS in background electrolyte solution).

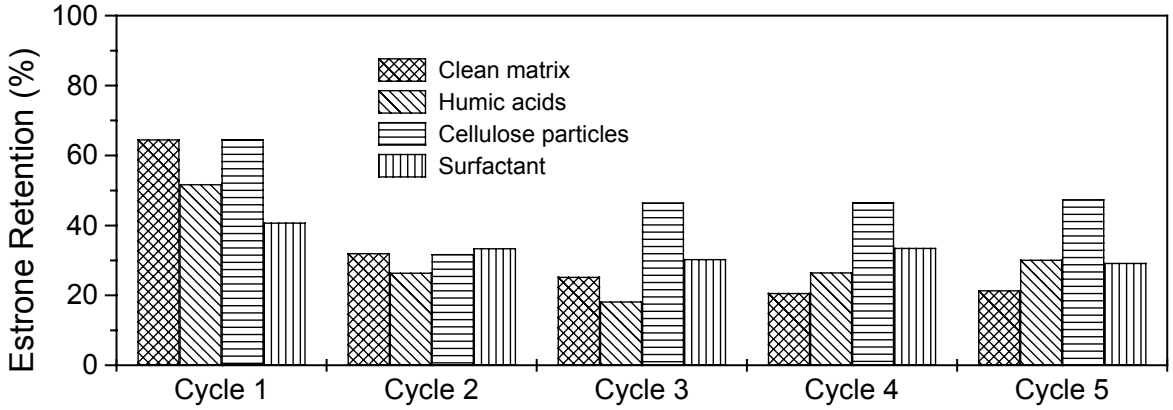


Figure 8.8: Estrone retention by the TFC-SR2 membrane at 5 filtration cycles at pH 12 (Clean background electrolyte contains 100 ng/L estrone, 20 mM NaCl, and 1 mM $NaHCO_3$; humic acid solution contains 20 mg/L of HAs, cellulose solution contains 60 mg/L of cellulose, and surfactant solution contains 1 mM SDS in background electrolyte solution).

Because the membrane has a finite adsorptive capacity, estrone retention decreases as the removal mechanism shifts from adsorption to size exclusion. At pH 6, it appears that adsorption (or the partitioning process) has been almost completed at the fifth cycle. Results reported in Figure 8.7 indicate that other constituents in the water matrix such as organic matter, colloidal particulates, and surfactant may influence the adsorption of estrone to the membrane and ultimately the removal efficiency to some degree. Estrone retention is considerably enhanced with the presence of organic particulates (cellulose) due possibly to the partitioning of estrone to cellulose particles [260]. In contrast, surfactant appears to reduce estrone adsorption and subsequently retention to a discernible extent. Further delineation of this phenomenon can be found in the following section. Surprisingly, estrone retention at the fifth filtration cycle is slightly lower with the presence of humic acid in the feed solution. This is probably attributed to the large pore size of the TFC-SR2 membrane. It is noted that as previously shown in section 3, the presence of organic matter did not result in any enhancement in estrone retention by the TFC-SR2 membrane. Nevertheless, in this particular case, the results appear to remain inconclusive.

At pH 12, retention is significantly reduced and adsorption appears to induce a negligible effect on retention after 2 or 3 filtration cycle. This is due to the deprotonation of estrone at high pH (above 10.4 – the pK_a value of estrone), which results in an unfavourable condition for adsorption of a negatively charged estrone molecule to the negative surface of the membrane [124]. It is also noteworthy that at pH 12, where adsorption is unfavourable, the presence of humic acid and

surfactant appears to insert an indiscernible impact on estrone removal in comparison to a clean water matrix. At the same pH, cellulose seems to enhance estrone retention to a small extent.

5.5 Estrone adsorption in the presence of other constituents

Figure 8.9 shows estrone retention at the first filtration cycle (conducted using a stirred cell) at different solution pH. At pH below 10.4, estrone removal is primarily governed by adsorption. On the other hand, at pH 12 where the deprotonation of estrone occurs, due to charge repulsion between the negatively charged estrone and negative surface of the membrane, adsorption is minimal, which translates into a considerably lower retention.

While the presence of cellulose and humic acids appears to have an indiscernible impact on estrone adsorption in the first filtration cycle, it is clear that estrone retention is markedly lower in the presence of surfactant (sodium docecyl sulfate) at all pH values (see Figure 8.9). This is consistent with the observation described in section 5.2. As discussed previously, surfactant may enhance the solubility of estrone in an aqueous solution or in other words reduce the apparent hydrophobicity of the compound. This can possibly result in a lower adsorption and therefore lower retention in the first filtration cycle. Results reported here are also consistent with a study by Oschmann et al. [266], where sodium dodecyl sulfate was reported to compete with organic matter for adsorption to ultrafiltration membranes.

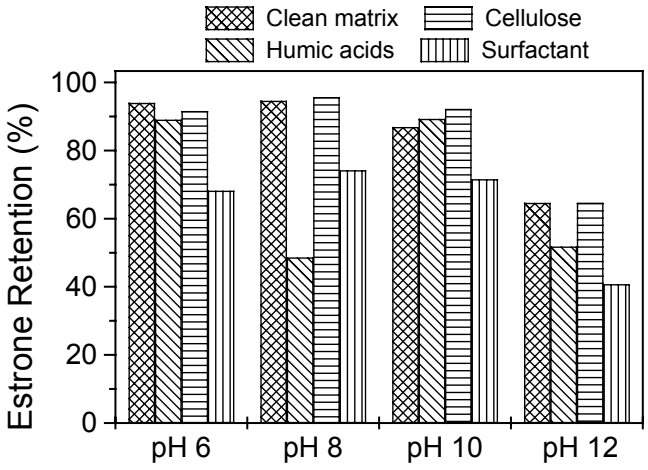


Figure 8.9: Effects of various constituents on estrone retention by the TFC-SR2 membrane in the first filtration cycle as a function of pH (clean background electrolyte contains 100 ng/L estrone, 20 mM NaCl, and 1 mM $NaHCO_3$; humic acid solution contains 20 mg/L of HAs, cellulose solution contains 60 mg/L of cellulose, and surfactant solution contains 1 mM SDS in background electrolyte solution).

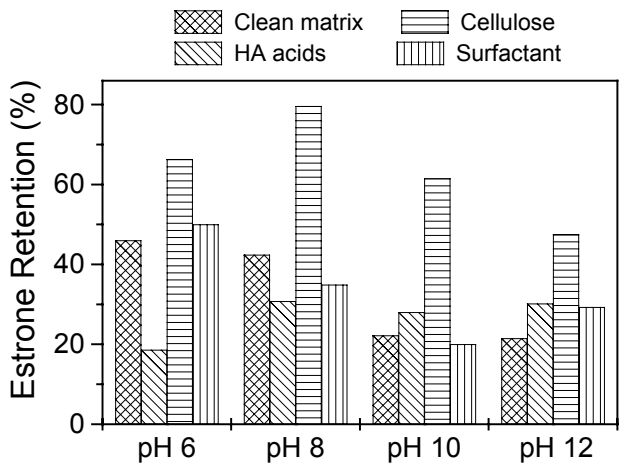


Figure 8.10: Effects of various constituents on estrone retention by the TFC-SR2 membrane in the fifth filtration cycle as a function of pH (clean background electrolyte contains 100 ng/L estrone, 20 mM NaCl, and 1 mM $NaHCO_3$; humic acid solution contains 20 mg/L of HAs, cellulose solution contains 60 mg/L of cellulose, and surfactant solution contains 1 mM SDS in background electrolyte solution).

Estrone retention at the fifth filtration cycle at different solution pH is presented in Figure 8.10. As discussed previously, at this stage estrone removal is governed mostly by size exclusion, although the diffusion of estrone that has previously adsorbed to the membrane may also influence the separation process to some extent. Similar to the phenomenon observed in Figure 8.8, the presence of humic acids and surfactant seems to have negligible impact on estrone retention at all pH values. It is noted in both cases, size exclusion is the dominating removal mechanism. In contrast, estrone retention is higher when cellulose particulates are present in the feed solution.

Cellulose particles are significantly larger than the membrane pore size and the accumulation of cellulose at the membrane surface will only result in a porous cake layer with negligible hydraulic resistance [266]. Consequently, retention enhancement observed here is not because of the pore blocking or pore restriction phenomena, as previously described for different foulants by Schäfer *et al.* [230]. Furthermore, because the cake layer formed by cellulose particle deposition on the membrane surface is quite porous, retention is unlikely to be affected by the cake-enhanced concentration polarisation phenomenon as reported by Ng and Elimelech [267]. In fact, the retention enhancement observed in this case is possibly attributed to the partitioning of estrone to cellulose particles [260], which are completely retained by the membrane. It is noteworthy that the cellulose concentration used in this case is 60 mg/L. This is significantly higher than the humic acid concentration, which is 20 mg/L as TOC. Molecular weight of SDS is 288 mg/L and TOC

measurement of the feed and permeate samples of several experiments indicate that it can easily pass through the membrane.

Since cellulose is an insoluble polysaccharide, partition of estrone into cellulose particles is likely to take place via hydrophobic interactions. Although hydrophobicity of cellulose particles is not available, their large particle size probably suggests a large area available for hydrophobic adsorption. At pH 12, due to the dissociation of estrone to become an anionic species, the compound becomes more hydrophilic. It has also been reported that cellulose particles become more negatively charged as the solution pH increases [268]. The combined effect would result in a decrease in adsorption (or partitioning) of estrone into cellulose particles, which is reflected in a lower retention at pH higher than 10.4 as can be seen in Figure 8.10.

5.6 Implication to full-scale applications

A full-scale membrane filtration process involves many operating variables including (but not limited to) cross flow rate, transmembrane pressure, recovery, cleaning frequency, module design, and system arrangement. Although this chapter did not examine every one of these variables, it has been demonstrated that some of these variables might have some certain effects to the overall removal efficiency as demonstrated in the case of transmembrane pressure. Therefore, it is essential that the translation of fundamental findings obtained from a laboratory condition experiment to a real life situation should take various operating variables into careful consideration.

A similar precautionary note can be emphasized on the solution chemistry. Effects of well defined parameters such as size of the solute, pH, and ionic strength on trace organic retention can be experimentally examined and theoretically presented in the form of mathematical models as illustrated in Chapter 4 and 5. Unfortunately, this premise may not be true for many constituents in the water matrix. Because of their heterogeneity, precise properties of many constituents are not available. As demonstrated in this chapter, the presence of organic particulate matter (represented by cellulose) could enhance retention via a co-filtration mechanism, in which estrone partly partitioned into cellulose particles that were retained completely by the membrane. In a separate study, the influence of colloidal fouling on trace organic retention via the so called “cake enhanced concentration polarisation” has also been methodically delineated by Ng and Elimelech [267]. It is perhaps due to the complexity of a real situation or the mechanisms in general, that very scattered data are often recorded from full-scale filtration plants.

6. *Conclusions*

The adsorption and diffusion process of trace organic estrone in the membrane polymer has probably dampened the effect of cross flow velocity while exacerbating the effect of transmembrane pressure on estrone retention. No retention variation was observed in the cross flow velocity range between 0.073 to 0.24 m/s in this study. In contrast, estrone retention decreased dramatically as the applied pressure increased.

The presence of other constituents in the feed solution may have some effects on trace organic retention. Surfactant reduced estrone adsorption to the membrane. However, the ultimate effect of surfactant on estrone retention remains inconclusive. Retention enhancement in the presence of organic matter was evident for reverse osmosis membranes, while this phenomenon was absent for the loose NF membrane TFC-SR2. Likewise, adsorption (or partitioning) of estrone to cellulose particles resulted in a small but discernible retention enhancement due to co-filtration as cellulose particles were completely retained by the membranes. In both cases, solute-particle or solute-organic matter interaction appears to play an important role in governing this effect.

Results presented in this chapter critically demonstrate the possible complexity of a real membrane filtration system where trace organic contaminants are of concern. Findings in previous chapters are fundamentally crucial in understanding the removal mechanisms and filtration processes of trace organic contaminants. However, the application of such findings to a real situation requires a careful consideration of operating variables, the solution chemistry, and major constituents that may be present in the feed solution.

Chapter 9

Conclusions

The necessity of water reclamation is growing, driven by a stress on water supply and public desire for a significant improvement in wastewater treatment. Numerous water reclamation schemes in regions with restricted freshwater resources for both non-potable and indirect potable purposes are currently on trial or even at an early stage of their full-scale operation. Nanofiltration (NF) and low-pressure reverse osmosis (RO) membranes are widely used in such schemes. There is no doubt that in the future, NF and low pressure RO membranes will continue to play a central role in propagating the success of water reclamation.

NF/RO membranes can produce superior treated water quality compared to conventional technologies based on most, if not all, current drinking water standards and guidelines. However, the current body of data concerned with trace organics removal by the NF/RO membranes are mostly related to pesticides. Given the gathering concern over environmental health impacts of emerging water and wastewater trace contaminants, this dissertation aimed to contribute towards the promotion of both water reclamation and the use of NF/RO membranes for the production of high water quality. The objectives of this dissertation were:

- to demonstrate the capacity and limitations of NF/RO membranes in removing emerging trace contaminants,

- to elucidate the removal mechanisms of trace contaminants by NF/RO membranes, and

- to identify key factors influencing the retention of trace contaminants by NF/RO membrane filtration processes.

The dissertation began with a thorough literature review to demonstrate the significance of the current available data and to identify critical points for subsequent investigation. This literature review was also regularly updated to include most recent findings relevant to this dissertation. A

comprehensive list of nine organic compounds representing three major groups of emerging trace contaminants, namely natural steroid hormones, hormone mimicking compounds, and pharmaceutically active compounds were selected for study. The research was conducted with 10 commercially available NF/RO membranes, although the bulk of the dissertation focused on the NF-270 and the NF-90 membranes. Both membrane characteristics and organic solute physicochemical properties were characterised and studied in great detail. Retention mechanisms were critically elucidated by relating the retention behaviours of trace organics to their physicochemical characteristics and the membrane properties.

The structure of this dissertation was based on major mechanisms of trace organic contaminant retention and transport through the NF/RO membranes: steric or size exclusion (Chapter 4), electrostatic or charge repulsion (Chapter 5), adsorption (Chapter 6), and sorption-diffusion transport (in Chapter 7). Chapter 8 provided some bridging links of the fundamental findings of this study to the real world by considering the complexity of the solution chemistry often encountered in practice.

A pore transport model that incorporated steric (size) exclusion and hindered convection and diffusion was used to characterise the membrane average pore size. This pore transport model was successfully used to predict the retention of low molecular weight inert (or non-adsorptive) and low dipole moment (negligible polarity effects) organic solutes for a given membrane pore size. The prediction played a central role in identifying and delineating the physicochemical properties, which can influence the separation process of trace organics by NF/RO membranes. Results reported in this dissertation indicate that natural hormones and hormone mimicking compounds can adsorb to the membrane to a considerable extent. At the early stage of filtration, adsorption (or partitioning) of hormones and hormone mimicking compounds to the membrane is the dominant removal mechanism. Because the adsorptive capacity of the membrane is limited, the final retention stabilized when the adsorption of hormones and hormone mimicking compounds to the membrane polymer has reached equilibrium. At this latter stage, the overall retention is lower than that expected based solely on the steric (size) exclusion mechanism.

The results also indicate the significance of polarity interaction for trace organics, which have a high dipole moment and are cylindrical in shape. For uncharged and non-adsorptive organic compounds with sufficiently high dipole moments (larger than 3), attraction between the molecule

polar centers and fixed charged groups of the membrane surface can direct the molecule to approach the membrane pores head on. Consequently, high dipole moment and cylindrical organics with a cylindrical shape may exhibit a much lower retention that that expected based on a size exclusion mechanism, where the molecule approaches the membrane pores randomly.

Employing the well-known TMS model for charged solutes, part of this dissertation explored the role of charge interaction in the separation of ionisable trace organics using NF membranes. Although limited to an ideal 1:1 electrolyte solution and the assumption that charge solute is considered as a point charge, the TMS model could be used to extensively and theoretically examine the effects of various solution chemistry and membrane properties on retention of anionic trace organics. Such findings were consistently supported by experimental data obtained with a steroid hormone, a hormone-mimicking compound, and two pharmaceuticals in their anionic forms. Retention behaviour of charged organics is quite similar to that of inorganic salts. Results obtained from the TMS model are in good agreement with data from the nanofiltration experiments of trace organics. The membrane charge density (represented by the membrane zeta potential) and average pore size are two critical parameters governing the separation process of charged trace organics. An increase in the solution ionic strength would suppress the Debye length, and hence, reduce the extent of charge repulsion. Ionic organic solutes do not adsorb to the membrane polymer, due primarily to electrostatic repulsion. Negatively charged trace organics exhibit high retention, even with the very loose TFC-SR2 membrane. It appears that the solute pH can have a dramatic effect on retention as it influences both the speciation of ionisable trace organics and the membrane surface charge density. The pH effect was most obvious for loose nanofiltration membranes when charge repulsion was the dominating retention mechanism.

Adsorption is inherent in any NF/RO membrane filtration process, particularly when trace organics are involved. Adsorption is primarily governed by both hydrophobic interaction and hydrogen bonding. Membrane characteristics such as surface roughness, membrane pore size, and hydrophobicity (represented by the membrane contact angle) can also play important roles in influencing the adsorption process. It was demonstrated that simple mass balance could be used to quantify adsorption of trace organics to the membranes. Linear adsorption isotherms were observed during both static (no applied pressure) and filtration adsorption experiments. Under a static condition, desorption occurred marginally, however, under a typical transmembrane pressure, significant desorption to the permeate side could be observed. It appears that adsorption is strongly

influenced by the solution pH and to a lesser extent by the presence of other organics in the bulk solution. In contrast, within a typical range of surface water and secondary treated effluent, ionic strength seems to have a negligible effect on adsorption. The reported results also demonstrated that the membrane could possibly serve as a large reservoir for EDCs and their release was possible during membrane cleaning or erratic pH variation during operation. Complete desorption of EDC to the membrane cleaning solution occurred at high pH, which was also typical of most cleaning solutions. This could result in a high concentration of EDCs in the spent cleaning solution. Results reported in this dissertation imply that treatment of the concentrate and the spent membrane cleaning solution should be carefully considered when EDCs are amongst the target contaminants in NF/RO membrane filtration. These results have a very important significance, as to date, risk implications in association with concentrate and membrane cleaning solution disposal have not been adequately addressed.

It has been demonstrated that under a dialysis condition, there was a small but apparent diffusion flux of certain trace organic contaminants (which were larger than the membrane pore size) across the polymeric membranes. The Rutherford Backscattering Spectroscopy technique was employed to measure the thickness of the membrane's active and supporting layers. The diffusion coefficients of estrone in the polyamide active layers of the three selected membranes were then determined. Results reported in this dissertation indicate that the diffusion coefficients of estrone in the active layers of these membranes were quite low. However, because their active layers were also very thin, the separation efficiency of certain trace organic contaminants could be strongly influenced by diffusion.

Operating condition and solution chemistry are important factors to consider when accessing the removal of trace organic contaminants by NF/RO membrane filtration processes. Results reported in this dissertation indicate that the sorption-diffusion process of trace organics in the membrane polymer has probably dampened the effect of cross flow velocity whilst exacerbating the effect of transmembrane pressure on retention. No estrone retention variation was observed in the cross flow velocity range between 0.073 to 0.24 m/s in this study. In contrast, estrone retention decreased dramatically as the applied pressure increased. It should, however, be noted that the observed phenomena can be complicated by a variation in the concentration polarization. The presence of other constituents in the feed solution may have some effects on trace organic retention. Surfactant reduced estrone adsorption to the membrane. However, the ultimate effect of surfactant on estrone retention remained inconclusive. Retention enhancement in the presence of organic matter was

evident for reverse osmosis membranes, while this phenomenon was absent for the loose NF membrane TFC-SR2. Likewise, adsorption (or partitioning) of estrone to cellulose particles resulted in a small but discernible retention enhancement due to co-filtration as cellulose particles were completely retained by the membranes. In both cases, solute-particle or solute-organic matter interaction appears to play an important role in governing this effect. The results presented also critically demonstrate the possible complexity of a real membrane filtration system where trace organic contaminants are of concern. Findings throughout the dissertation are fundamentally crucial in understanding the removal mechanisms and filtration processes of trace organic contaminants. However, the application of such findings to a real situation requires a careful consideration of operating variables, the solution chemistry, and major constituents that may be present in the feed solution.

This dissertation provides a rich and conclusive body of evidence, upon which answers for the research questions of the dissertation laid out previously could be drawn. The effectiveness of tight NF and RO membranes in removing all trace organics selected in this study was clearly demonstrated. Retention of these trace organics by the tight NF-90 membranes were high in all experimental conditions. However, adsorption of some trace organics to the membrane polymer represented a critical issue not only with the filtration process itself, but also with regards to the treatment and discharge of the concentrate and spent membrane cleaning solution.

Trace organic retention by the loose NF membranes depended strongly on the experimental conditions, the contaminant physicochemical properties, and the membrane characteristics. In a nutshell, the mechanisms of trace organic retention and transport through NF (and RO) membranes can be schematically summarised in Figure 9.1. Retention of negatively charged trace organic contaminants is governed by both electrostatic and steric exclusions. The separation is effective and high retention can be achieved even with quite loose NF membranes.

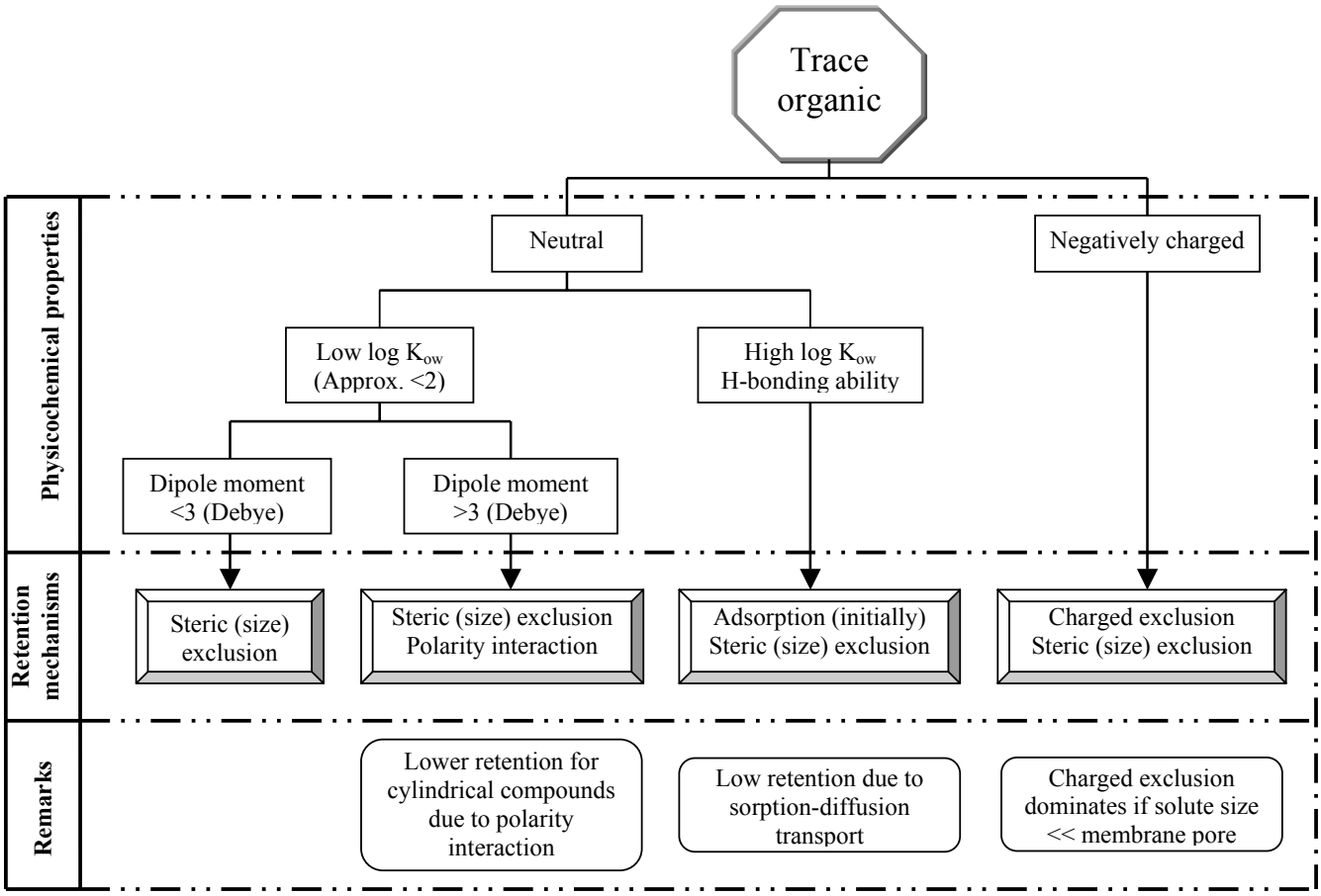


Figure 9.1: Mechanisms of retention and transport of trace organics in NF/RO filtration processes based on solute physicochemical properties and typical membrane characteristics.

Steric (size) exclusion is solely responsible for the retention of uncharged organic species. For such contaminants, intrinsic physicochemical properties of the trace organic molecules are key factors influencing their separation processes (Figure 9.1). Trace organic contaminants with high hydrophobicity (represented by their log K_{ow}) and an ability to form Hydrogen-bonding can absorb to the membrane polymer and subsequently diffusion through the membrane. This phenomenon often results in a lower retention than that of an inert (non-adsorptive) compound of similar size. For uncharged and non-adsorptive organic compounds with sufficiently high dipole moments (larger than 3), attraction between the molecule polar centers and fixed charged groups of the membrane surface can direct the molecule to approach the membrane pores head on. Consequently, high dipole moment and cylindrical organics with a cylindrical shape may exhibit a much lower retention that that expected based on size exclusion mechanism, where the molecule approaches the membrane pores randomly.

Chapter 10

Further Research

Scientific knowledge has no boundary. Naturally during the process of conducting this research and discussion with colleagues, new ideas emerged. Findings reported in this dissertation are critical and have revealed new scope for further fundamental as well as applied research works. In a fundamental aspect, the following areas can be of particular interest: modeling and predicting retention of trace organics by NF/RO membranes; concentrate and spent membrane cleaning solution treatment and discharge; effects of various type of fouling on the removal efficiency, particularly biofouling and organic fouling; and novel system and membrane designs. In a practical aspect, it is essential to collect data from pilot and large-scale membrane filtration plants where emerging trace organic contaminants are of concern to verify and appreciate the complexity of a large-scale application.

A comprehensive and mechanistic model capable of predicting the performance of NF/RO membranes with regard to emerging trace organic contaminants will be an indispensable tool for the water industry in dealing with these contaminants. Such models exist for uncharged and inert organic solutes (Chapter 4) and for salts or ionic species (Chapter 5). Factors influencing the separation processes have also been revealed. The challenge to be overcome in this case is perhaps how to combine them in a harmonised fashion to take into account the speciation of several trace organics and their changing physicochemical properties accordingly. It is also essential to address the scarcity of information related to physicochemical properties of trace organic contaminants and the homogeneity of the membrane polymeric materials.

As previously discussed throughout this dissertation and particularly in Chapter 6, the treatment and discharge of concentrate and spent membrane cleaning solution are critical in the management, design and operation of the membrane filtration works. Waste minimisation, concentrate characterisation, toxicological investigation, treatment technologies capable of dealing with concentrate and spent cleaning solution are amongst the list of possible studies to address this issue. In fact, concern over concentrate treatment is rising, driven in part by the occurrence of emerging

trace organic contaminants and inland applications of many membrane filtration plants for water reclamation purposes. It is expected that this particular issue will be the focus of many membrane researchers for years to come as the number and size of water reclamation plants increases.

Fouling is an inevitable phenomenon in most (if not all) of the membrane filtration processes. It is known to strongly influence not only the production of clean water but also contaminant removal efficiency by the membranes. Numerous dedicated investigations have been devoted to study the fouling effects on the retentions of various contaminants. However, studies addressing the particular issues related to emerging trace organic contaminants remain very scarce [267]. Most emerging trace organic contaminants are biologically active and can interact quite strongly with other macromolecules. Consequently, investigation elucidating the influence of both biofouling and organic fouling on their retention will create interesting results.

Novel concepts in both membrane and system designs can be used to enhance the technological capability and mitigate shortcomings. To some degree, this is related to the operation of the membrane systems, treatment and discharge of the concentrate and spent membrane cleaning solution. Module design, new membrane materials and new system arrangements are progressively improving the performance of membrane filtration processes in its broader context. It is expected that such improvements can also be used for a more effective emerging trace organic removal. Indeed, as this chapter is being written, a novel affinity membrane capable of distinguishing estradiol from another nearly identical steroid hormone estrone has just been reported [269]. In a dynamic filtration process, this membrane retained 99% of estradiol via specific binding.

There has been an astonishing amount of progress and development in the field of analytical and environmental chemistry, reflected strongly by the ability to detect and quantify a trace amount of contaminants down to less than a nanogram per liter (ng/L) level. Given the complexity involved in full-scale applications, data available from existing ones will provide an essential tool to verify and to apply fundamental findings from this dissertation as well as from other similar research works to improve performance. Surprisingly, data related to emerging trace organic contaminants collected from both pilot and full-scale membrane filtration plants remain particularly scarce in the open literature. Perhaps a major impediment for many data collection studies is the slow diffusion of the available analytical techniques required for such studies and the level of laboratory skills associated with these dedicated techniques. While this is also attributed to the fact that data collections are still in progress in several newly operating water reclamation schemes, the interpretation and continuous

collection of such data remains an essential issue, one that will continue to attract special attention from the scientific community and the membrane industry.

Driven by the desire for a better water quality and the need for augmentation of water supplied with wastewater reuse, trace contaminant removal has become an important feature of nanofiltration and reverse osmosis membrane filtration processes. The list for further research is not exhaustive and a lot more research will be needed at both fundamental as well as practical levels. New contributions to this progress for the betterment of our water supply and the environment will be warmly welcomed.

Glossary

ACN	Acetonitrile
APEs	Alkylphenol ethoxylates
AFM	Atomic force microscope
ANSTO	Australian nuclear science and technology organisation
BPA	Bisphenol A
BSA	Bovine serum albumin
CP	Concentration polarisation
DI	Deionised water
DBPs	Disinfection by-products
DOC	Dissolved organic carbon
EfOM	Effluent organic matter
EDCs	Endocrine disrupting chemicals
FA	Fulvic acids
HAAs	Halogenated acetic acids
HPLC	High performance liquid chromatography
HA	Humic acids
ICP-AES	Inductive couple plasma - Atomic emission spectroscopy
IBA	Ion beam analysis
IEP	Isoelectric point
MCLs	Maximum contaminant levels
MW	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
NOM	Natural organic matter
NPOC	Non purgeable organic carbon
NP	nonylphenol
POPs	Persistent organic pollutions
PhACs	Pharmaceutical active compounds
PAHs	Polyaromatic hydrocarbons
PCBs	Polychlorinated biphenols
RO	Reverse osmosis
RBS	Rutherford backscattering spectroscopy
SEM	Scanning electron microscope
SOCs	Sewage treatment plant
SDS	Sodium dodecyl sulfate
SMX	Sulfamethoxazole
SRNOM	Suwannee river natural organic matter
STP	Synthetic organic compounds
TMS	Teorell-Mayer-Sievers model
TBP	Tert-butyl phenol
TFC	Thin film composite
TFU	Thin film unit
TOC	Total organic carbon
TOX	Total organic halide
TOXFP	Total organic halides formation potential
TEM	Transmission electron microscope
THMFP	Trihalomethanes
THMs	Trihalomethans formation potential
UF	Ultrafiltration
WWTPs	Wastewater treatment plants

List of Symbols

Chapter 2

c	concentration (g/L)
c	concentration in solution (g/L)
c_m	concentration in membrane phase (g/L)
D_s	solute diffusion coefficient in water (m^2/s)
E_{don}	Donnan potential (V)
F	Faraday constant (96 500 C/mol)
J	volume flux (m/s)
k	Boltzmann constant ($1.38 \cdot 10^{-23}$ J/K)
M	molecular weight (g/mol)
q	electric charge (esu)
R	gas constant (8.314 J/mol.K)
r,x	distance (m)
T	temperature (^oK)
T	temperature (K)
V_s	solute molar volume (cm^3/mol)
V_w	water molar volume (cm^3/mol)
z	charge number (-)
δ_s	solute surface tension (N/m^2)
δ_w	water surface tension (N/m^2)
η	viscosity (cP)
μ	dipole moment (Debye)

Chapter 4

C	total molar concentration (mol/m^3)
C_b	solute concentration in the bulk solution (mol/m^3)
C_m	solute concentration at the membrane surface (mol/m^3)
C_p	solute concentration in the permeate (mol/m^3)
C_s	solute concentration (mol/m^3)
δ	concentration polarisation layer thickness (m)

D_1,D_2	over all transport coefficient (m^2/s)
$\Delta\Pi$	transmembrane pressure (kPa)
D_{sm}	diffusion coefficient in membrane phase (m^2/s)
D_{sw}	diffusion coefficient in water (m^2/s)
ε	membrane porosity (-)
ϕ	distribution coefficient (-)
γ_σ	solute activity coefficient (-)
H	hindrance factor for diffusion (-)
J_s	solute flux (mol/m^2)
J_v	water flux (m/s)
K_c	hindrance coefficient for convective transport (-)
K_d	hindrance coefficient for diffusive transport (-)
k_f	mass transfer coefficient (m/s)
L	membrane (active layer) thickness (m)
λ	solute radius over pore radius ratio (-)
P	solute permeability (mol/m^2s)
Pe	membrane Peclet number (-)
P_h	hydraulic (water) permeability (m/s)
R_o	observed retention (-)
r_p	pore radius (m)
R_r	real retention (-)
r_s	solute radius (m)
σ	reflection coefficient (-)
S_a	sieving coefficient (-)
V	solute velocity along the membrane pore (m/s)
W	hindrance factor for convection (-)
x_m	solute mole fraction in the membrane polymer (-)
x_s	solute mole fraction in aqueous (-)

Chapter 5

ψ	electro potential of the surface (V)
$1/\kappa$	Debye length (nm)
D_{si}	diffusion coefficient of component i (m^2/s)
ε	relative dielectric constant of water (-)
ε_0	permittivity of vacuum (-)

F	Faraday constant (9650 C/mol)
I	ionic strength of the bulk solution (mol/m^3)
I_{cur}	electric current (A)
J_i	total flux of component i (mol/m^2)
$J_{i,conv}$	solute flux of component i due to convection (mol/m^2)
$J_{i,diff}$	solute flux of component i due to diffusion (mol/m^2)
$J_{i,elec}$	solute flux of component i due to electro potential (mol/m^2)
J_v	water flux (m/s)
q_0	dimensionless electrical potential (-)
q_w	membrane surface charge density (C/m^2)
R	gas constant (8.314 J/mol.K)
r	distance from the membrane pore center line (m)
T	temperature (K)
x	distance from the charged surface (m)
X	volume charge density (c/m^3)
z	electro chemical valence number of the ion (-)

Chapter 6

1/n	adsorption intensity (-)
A	membrane area (m^2)
B	Langmuir constant (-)
C_{eq}	equilibrium concentration of the adsorbate in aqueous phase (mol/m^3)
C_F	feed concentration (mol/m^3)
C_P	permeate concentration (mol/m^3)
C_{Spent}	concentration in the spent membrane cleaning solution (mol/m^3)
ϕ	membrane-solute energy potential (J)
ϕ_Δ	dispersion energy (J)
F_F	feed flow rate (m^3/s)
$\phi_{\Phi\mu}$	interaction energy between permanent dipoles
F_P	permeate flow rate (m^3/s)
ϕ_P	repulsion energy (J)
$\Gamma_{\theta\varepsilon}$	equilibrium concentration of the adsorbate in the solid phase (mol/m^3)
$\Gamma_{\xi\alpha\mu}$	concentration of the adsorbate in the solid phase at saturation (mol/m^3)
K	adsorption capacity (-)

r	distance between adsorbate and adsorbent (m)
Rec	Recovery (-)
Ret	Retention (%)
V	volume (m^3)
V_C	concentrate volume (m^3) or concentrate volume flow rate (m^3/s)
V_F	feed volume (m^3) or feed volume flow rate (m^3/s)
V_P	permeate volume (m^3) or permeate volume flow rate (m^3/s)

Chapter 7

A	membrane area (m^2)
C_{mI}	solute concentration in the membrane at the feed side (mol/m^3)
C_{mII}	solute concentration in the membrane at the permeate side (mol/m^3)
D	diffussion coefficient in the membrane (m^2/s)
Δx	membrane active layer thickness (m)
J	solute flux (mol/m^2)
S	partition coefficient (-)
t	diffusion time (s)
V_I	volume of the donor compartment (m^3)
V_{II}	volume of the acceptor compartment (m^3)

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Thesis Related Publications

Refereed Journal Papers

1. **Nghiem, L.D.,** Schäfer, A.I., Elimelech, M. "Nanofiltration of Hormone Mimicking Trace Organic Contaminants", *Separation Science & Technology* (In press, Accepted July 2005).

2. **Nghiem, L.D.,** Schäfer, A.I. "Factors influencing adsorption and release of EDCs in NF/RO filtration processes", *Desalination* (In press, Accepted June 2005).

3. **Nghiem, L.D.,** Schäfer, A.I., Elimelech, M. "Pharmaceutical Retention Mechanisms by Nanofiltration Membranes", *Environmental Science & Technology* (2005) 39, 7698-7705.

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7. **Nghiem, L.D.,** Schäfer, A.I., Waite, T.D. "Membrane filtration in water recycling: removal of natural hormones", *Water Supply* (2003) 3, 3, 155-160.

8. Schäfer, A.I., **Nghiem, L.D.,** Waite, T.D. "Removal of Natural Hormone Estrone from Aqueous Solutions using Nanofiltration and Reverse Osmosis", *Environmental Science & Technology* (2003) 37, 182-188.

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Book Chapters

1. **Nghiem, L.D.,** Schäfer, A.I. "Trace contaminant removal with nanofiltration" in Nanofiltration - Principles and Applications, A.I. Schäfer, A. Fane, and D. Waite, Editors. 2004, Elsevier Science. Chapter 20, 479-520.

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2. **Nghiem, L.D.,** Schäfer, A.I., Elimelech, M. "Mechanisms of steroid hormones and hormone mimicking compounds removal in nanofiltration", *World water congress* 2004. Marrakech, Morocco.

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12. Schäfer, A.I., **Nghiem, L.D.** "Charge Interactions, Adsorption and Size Exclusion as Mechanisms in Organics Removal using Reverse Osmosis and Nanofiltration", *IWA Meeting Mülheim*, Germany, September 2002, CD Rom, 333-341.

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3. **Nghiem, L.D.,** Schäfer, A.I., Elimelech, M. "Solute membrane affinity effects on nanofiltration of steroid hormones and pharmaceutically active compounds", *Gordon Research Conference*, August 1-6, 2004, USA, New London, NH.

Appendix 1

HPLC Mobile Phase Gradient Program

Acetonitrile and water were used the mobile phase for the HPLC analysis of the hormone mimicking compounds. A similar eluent program was used for all three compounds – nonyl phenol, bisphenol A, and tert-butyl phenol (Table A1.1). The UV detection wave length was 280 nm for all of these compounds.

Table A1.1: Eluent program for the HPLC analysis of nonyl phenol, bisphenol-A, and tert-butyl phenol.

Time	Component	Action
0.01	Eluent A Composition	70%
12.00	Eluent A Composition	70%
12.01	Eluent A Composition	70%
14.00	Rinse	
24.00	Eluent A Composition	20%
24.01	Eluent A Composition	0%
30.00	Eluent A Composition	0%
30.01	Eluent A Composition	70%
35.00	Stop	

Eluent A: 100% water.
Eluent B: 100% Acetonitrile.

Acetonitrile and water were used the mobile phase for the HPLC analysis of pharmaceuticals. The eluent was buffered with 0.025 mM KH_2PO_4 (pH ~ 4.5). and was premixed to ensure a homogeneous mobile phase. The eluent programs used for the analysis of sulfamethoxazole, carbamazepine, and ibuprofen are showed in Table A1.2, Table A1.3, and Table A1.4, respectively. The eluent was premixed to ensure a homogeneous mobile phase. Eluent A contained 20% Acetonitrile and 80% water; eluent B contained 80% Acetonitrile and 20% water. The UV detection wavelength for sulfamethoxazole and carbamazepine was 280 nm and for ibuprofen was 225 nm.

Table A1.2: Eluent program for the HPLC analysis of sulfamethoxazole.

Time	Component	Action
0.01	Eluent A Composition	50%
7.00	Eluent A Composition	50%
12.00	Eluent A Composition	20%
14.00	Rinse	
15.00	Eluent A Composition	50%
25.00	Stop	

Table A1.3: Eluent program for the HPLC analysis of carbamazepine.

Time	Component	Action
0.01	Eluent A Composition	100%
5.00	Eluent A Composition	100%
8.00	Eluent A Composition	40%
10.00	Eluent A Composition	40%
11.00	Eluent A Composition	100%
14.00	Rinse	
25.00	Stop	

Table A1.4: Eluent program for the HPLC analysis of ibuprofen.

Time	Component	Action
0.01	Eluent A Composition	50%
7.00	Eluent A Composition	50%
12.00	Eluent A Composition	20%
14.00	Rinse	
15.00	Eluent A Composition	50%
25.00	Eluent A Composition	

Appendix 2

Adsorption of non-labelled compounds

To verify the effect of tritium on the adsorption process when tritium labelled compounds were used, a set of experiments were carried out using non-labelled estrone. Stirred cell filtration experiments were conducted using the TFC-SR2 membrane at different solution pH. The feed concentration was 200 μg/L of estrone. Estrone adsorption per membrane surface area (cm^2) for non-labelled estrone was analytically measured using the procedure described in page 126. At the end of each filtration experiment, the membranes were cut into small pieces and placed in a scintillation vial to which 5 mL of acetone was added. The vial was shaken vigorously and left for 1 hour for all estrone to dissolve. 0.5 mL of solution was then extracted into another vial, which was air dried, then dissolved with 5 mL of methanol. A Shimadzu HPLC was used for the analysis of estrone. The result together with the result obtained with radiolabelled estrone (feed concentration of 100 ng/L of estrone) are shown in Figure 2A.1.

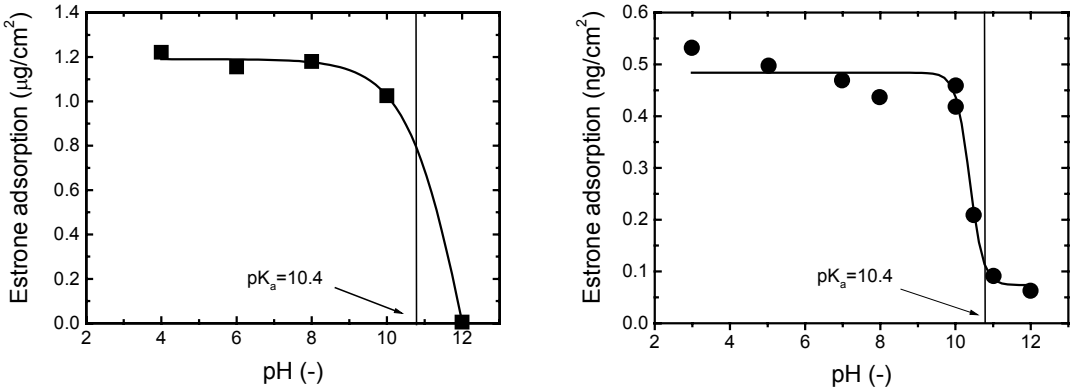

Figure A2.1: Adsorption of radiolabelled (circle) and non-labelled estrone (square) to the TFC-SR2 following stirred filtration experiments as a function of the solution pH. Feed solution contains 20 mM NaCl, 1 mM $NaHCO_3$, 100 ng/L of labelled estrone or 200 μg/L of non-labelled estrone.

The experiments with non-labelled estrone were conducted at a much higher feed concentration due to analytical difficulties. However, variation in the solution pH resulted in an identical adsorption phenomenon in both cases where no or minimal adsorption could be observed at pH higher than the pK_a value of the compound. Radiolabelled compounds have long been employed for various studies to a significant extent. Deuterated compounds are common used as internal standards in

analytical techniques. Studies investigating the removal of trace organics by NF/RO membranes using tritium[1] labelled compounds and ^{14}C [2] have also been reported. The bulk of the current scientific literature overwhelmingly indicates that radiolabelled compounds are identical to non-labelled one in their chemical behaviour.

[1] Yoon, Y., P. Westerhoff, J. Yoon, and S.A. Snyder, *Removal of 17β Estradiol and Fluoranthene by Nanofiltration and Ultrafiltration.* Journal of Environmental Engineering, 2004. **130**(12): p. 1460-1467.
[2] Chian, E.S.K., W.N. Bruce, and H.H.P. Fang, *Removal of Pesticides by Reverse Osmosis.* Environmental Science & Technology, 1975. **9**(1): p. 52-59.